

DEPARTMENT OF THE INTERIOR

ALBERT B. FALL, SECRETARY

U.S. BUREAU OF MINES

H. FOSTER BAIN, DIRECTOR

Engineering

INVESTIGATIONS OF ZIRCONIUM WITH ESPECIAL
REFERENCE TO THE METAL AND OXIDE

HISTORICAL REVIEW AND BIBLIOGRAPHY

BY

J. W. MARDEN and M. N. RICH



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INVESTIGATIONS OF ZIRCONIUM, WITH ESPECIAL REFERENCE TO THE METAL AND OXIDE. HISTORICAL REVIEW AND A BIBLIOGRAPHY.

By J. W. MARDEN and M. N. RICH.

INTRODUCTION.

That there is wide interest in the preparation and properties of metallic zirconium and its salts is indicated by the many articles recently published in scientific and technical journals and the many patents issued. The compounds of zirconium have numerous important uses and more uses will doubtless be found. In the course of the special work on rare metals that were of military importance during the war, the authors of this bulletin were detailed to the Golden mining experiment station of the Bureau of Mines to prepare metallic zirconium and to investigate its properties.

A number of investigations in recent years have indicated that sintered or coherent zirconium metal is very resistive to acids; that it can be used for electrodes, and it probably will find metallurgical uses. A steel containing zirconium has been proposed for use in armor plate and automobile parts, and nickel-zirconium alloys have been suggested for high-speed cutting tools and for cutlery. Numerous articles in scientific journals have recommended the use of zirconium oxide as a refractory, an abrasive, a pigment in paints, and as an opaquing agent in enamel ware. The salts have been used in the textile industry as a mordant and also for weighting silk.

When the authors began their investigation, they found it necessary to collect all of the available literature on the general subject of zirconium and its compounds. Pure salts could not be obtained on the market, and in order to get these, as a preliminary step to the preparation of the metal, the literature had to be classified and the methods of preparing the salts investigated. Also, there was much difficulty at first in making satisfactory analyses, and this phase of the work received careful attention.

As it was necessary to begin with a historical review of the literature, such a review is given as Part I of this report, and a bibliography is included as Part IV. References to the numbered items in this bibliography are made throughout the text, the usual

footnote references being omitted. Analyses of the products and conclusions as to their purity are given under the descriptions of methods of preparation. A table showing the properties of the amorphous metal, and another showing the properties of the coherent metal, will be found under appropriate headings in Part II.

No attempt has been made in the historical review to discuss fully all the published information about zirconium and its compounds, but only such material has been assembled as has a direct bearing upon the present work. Considerable difficulty was experienced in collecting this material because of the confusion of terms by various authors who perhaps did not thoroughly understand the chemistry of zirconium.

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PART I.—HISTORICAL REVIEW OF THE CHIEF MINERALS, THE SALTS OF ZIRCONIUM, AND ZIRCONIUM METAL.

CHAPTER I.—ZIRCONIUM MINERALS.

Many of the larger textbooks of chemistry give fairly good descriptions of the occurrence of zirconium, chiefly as zircon, the silicate, and as baddeleyite, the oxide. Browning⁷ gives the following table of zirconium minerals and formulæ:

TABLE 1. *Zirconium minerals and their formulæ.*

	ZrO ₂ per cent.
Zircon, ZrSiO ₄	61 to 67
Rosenbuschite, 6CaSiO ₃ .2Na ₂ ZrO ₂ F ₂ . (TiSiO ₃ .TiO ₂)	18 to 20
Lavenite, R(Si,Zr)O ₃ .Zr(SiO ₃) ₂ .RTa ₂ O ₅	28 to 32
Wohlerite, 12R(Si,Zr)O ₃ .RNb ₂ O ₅	15 to 23
Hortdahlite, 4Ca(Si,Zr)O ₃ .Na ₂ ZrO ₂ F ₂	21 to 22
Eudialyte, Na ₁₃ (Ca,Fe) ₅ Cl(Si,Zr) ₃ O ₂	11 to 17
Catapleiite, H ₄ (Na ₂ ,Ca)ZrSi ₃ O ₇	29 to 40
Elpidite, H ₆ Na ₂ ZrSi ₅ O ₁₅	20 to 21
Eucolite, see eudialyte	12 to 17
Auerbachite, see zircon	38 to 60
Cyrtolite, see zircon	60 to 67
Alvite, see zircon	48 to 51
Tritomite, complex silicates	1 to 2
Erdmannite, complex silicates	0 to 5
Polymignite, 5RTiO ₅ .5RZrO ₂ .R(Nb,Ta) ₂ O ₅	29 to 30
Arrhenite, complex	3 to 4
Sipylite, complex	2 to 3
Zirkelite (CaFe)O.2(Zr,Ti,Th)O ₂	52 to 53
Baddeleyite, ZrO ₂	96.5

Zircon is found in considerable amounts in many placer deposits derived from disintegration of granitic and pegmatic rocks. The best-known deposits in the United States are near Green River, Henderson County, N. C., and in the Wichita Mountains, near Cache, Okla. According to Iddings⁶⁰, zircon is found most abundantly in certain syenites of Norway, and occurs in crystalline limestone at Grenville and elsewhere in Canada. Dana²⁵ states that zircon occurs in various localities in North America, including Litchfield, Me.: Essex County, Orange County, and in St. Lawrence County, N. Y.: near Reading, Pa.: abundantly in the gold sands of Burke, McDowell, Polk, Rutherford, Henderson, and other counties in North

Carolina: with astrophyllite, etc., in the Pikes Peak region in El Paso County, and at Cheyenne Mountain, Colo. In California and elsewhere it occurs in auriferous gravels.

Baddeleyite (brazilite) is found in large deposits in Sao Paulo, Brazil. According to Schaller¹⁰⁹ this mineral has also been identified in Ceylon, Sweden, Italy, and Montana. Samples of zircon sand from Pablo Beach, Fla., have been investigated, and recently as much as 3 per cent of some of the auriferous sands of Idaho has been found to be zircon mixed with some monazite.

MINING AND CONCENTRATION OF ORES.

Meyer^{88a} gives an excellent discussion of the mining and concentration of Brazilian deposits of zircon and baddeleyite. According to him, zirconia ore is roughly divided into two classes:

First, alluvial pebbles ranging in size from $\frac{1}{2}$ to 3 inches in diameter, generally carrying about 90 to 93 per cent zirconium oxide. These pebbles, known as "favas" and having a specific gravity ranging from 4.8 to 5.2, are found along small stream beds and on the talus slopes of low ridges.

Second, zirconia ore proper, or zirkite, which ranges in shade from a light gray to a blue black, the lighter colored material carrying a higher percentage of zirconium silicate, as evidenced by analysis, which in some cases shows a minimum of 73 per cent zirconium oxide. The blue-black ore generally carries from 80 to 85 per cent zirconium oxide. By careful sorting, however, a uniform grade carrying about 80 per cent is produced. Prior to the investigations of Derby and Lee this ore was considered identical with baddeleyite. It has not been shown, however, that it is a mechanical mixture of three minerals, namely, brazilite, zircon, and a new and unnamed zirconium silicate carrying about 75 per cent zirconium oxide. This new mineral has the same crystal form as zircon (67 per cent ZrO_2), but is readily soluble in hydrofluoric acid, while zircon is not affected, this being a characteristic differential test. The finely powdered mineral, on being treated with a weak solution of hydrofluoric acid, leaves a residue of minute, perfect, pyramidal crystals of zircon, the brazilite and new zirconium silicate going into solution. Several large outcrops of the ore occur on the extreme westerly edge of the plateau, one or two isolated boulders weighing as much as 30 tons. No extensive development work has yet been attempted, although several crosscuts have been run to determine the width of the vein and a few shallow prospect holes to determine the depth, but seemingly through indifference of the owners this development work was not completed. Owing to the hardness of the ore it is almost impossible to drill holes for explosives, and in handling large masses it is found necessary to resort to the primitive methods employed by the emery miners of Nazos. A large fire is built against an exposed face of the ore and kept burning for several hours, at the end of which time water is thrown upon the ore, which produces fracturing of the mass, permitting it to be sledged into pieces easily handled by one man. In some of the deposits the ore occurs in the form of gravel and large pebbles embedded in a reddish clay matrix greatly resembling a boulder clay. This is mined by open-cut methods. The clayey mass, on being exposed to the tropical sun and air, readily dries and zirconia can then be separated from the clay matrix by a coarse screen. Before shipment it is thoroughly washed to remove the small percentage of ferruginous matter still adhering.

Most of the mines are many miles from the railroad. Horses for other than saddle purposes are practically unknown, and the ore is transported to the railroad station by ox carts carrying about 1 ton each. These carts are of the most primitive character, having large, solid, wooden wheels, some 4 feet in diameter and 6 inches in thickness. From 10 to 15 yoke of oxen (20 to 30 oxen) are generally required for each cart, owing to the mountainous roads.

This very cursory examination of the zirconia deposits makes it unsafe to venture any conjecture as to the quantity of ore available. Suffice it to say, however, that the deposits have been traced for a distance of 15 miles between Cascata and Caldas and, if surface indications are of any significance, are of vast extent.

In the concentration of zircon from zircon or monazite sand, the sand is usually passed over magnetic separators. The monazite is separated by the strongest magnet, the ilmenite by the intermediate magnet, and the magnetite by the weakest. Zircon is recovered in the tailings. The sands of the Pablo Beach deposits are put through magnetic separators, and the tailings, consisting of zircon, free silica, and appreciable percentages of titania (probably rutile), are passed over a Wilfley table and zircon of a fairly good concentration is obtained.

Anderson^{394b} says of the ores of titanium:

The most important industrial ores still continue to come from the deposits in the States of Minas-Geraes and Sao Paulo. No production of zirconium ores has been reported in the United States for several years, although formerly some came from North Carolina. Metallurgical ore [in 1918] sold at \$100 to \$140 for 80 per cent ZrO_2 , minimum.

Meyer⁸⁸ says that—

The year 1918 witnessed an unprecedented demand for zirkite—the commonly accepted trade name for native zirconium oxide. The total amount of zirkite imported in 1918 was approximately 1,400 gross tons. This ore carries 75 per cent to 80 per cent zirconium dioxide. This importation in 1918 is greater than that of any previous year. In 1913, 1,119 tons were imported, with a value of \$54,767. In other years smaller quantities were imported from Brazil.

The production in the United States has been small, reaching a maximum in 1883 of 26 tons. Since then the production has diminished up to the present time, when practically none is produced.

CHAPTER II.—TREATMENT OF ORE FOR THE RECOVERY OF ZIRCONIUM.

To recover the ZrO_2 from zircon and baddeleyite, it is customary to fuse the mineral. Prolonged digestion under pressure with hot concentrated H_2SO_4 will disintegrate some zirconium minerals, but according to many authors fusion mixtures are much to be preferred.

The principal fusion mixtures used are as follows:

1. $NaHSO_4$, $KHSO_4$, commercial niter cake, or pyrosulphates.
2. Caustic soda, soda ash, and sodium fluoride or sodium peroxide.
3. KHF_2 , $NaHF_2$ or HF .
4. Ignition with charcoal, subsequent chloridizing.
5. Electric-arc fusion of zircon, CaO , and C , leaching with H_2O and acid chloridizing residue.

FUSION WITH PYROSULPHATES, ACID SULPHATES, OR NITER CAKE.

The first of these general methods, suggested by Franz,¹⁸⁵ is in many respects one of the best commercial methods of obtaining the zirconium salts in solution. The quantity of fusion material used is preferably about 20 parts to 1 of the mineral. Any proportion less than 10 to 1 does not give as complete or as clear a fusion as might be desired. Most of the silica is made insoluble, but approximately 3 to 4 per cent of the silica is carried over with the soluble salts. The fusion is conducted in a graphite, silica, or cast-iron crucible. With 20 parts of the pyrosulphate or acid sulphate the temperature of fusion is relatively low, and an ordinary gas or oil muffle furnace will answer. The fusion can best be performed by sifting the ore (200-mesh) over the surface of the fused niter cake: this procedure minimizes the frothing of the mass. After the last of the ore has been sifted in, the fusion is conducted until the mass is a low cherry red; as the fusion is liable to go dry before this point is reached, the addition, as needed from time to time, of more niter cake or acid sulphate is advisable.

Zirconium is obtained in solution from the fusion in two ways: In the first the cake is covered with concentrated H_2SO_4 and heat until entirely dissolved; on cooling, the clear liquid is poured into cold H_2O , and resulting solution filtered nearly free of silica. The filtrate is then ready for the recovery of the zirconium salts.

In the second method the cooled fusion is digested in hot H_2O , and the insolubles and silica are filtered off as before. The zirconium is in the filtrate in the form of sulphate, or zirconyl sulphate, with silica, iron, aluminum, and much sodium sulphate.

FUSION WITH CAUSTIC SODA AND SODA ASH.

The caustic-soda and soda-ash fusions first used by Klaproth⁷⁰ and Berzelius³ are largely used in treating zirconium ores. In using caustic soda the proportions mentioned in the literature range from 4 to 8 parts of NaOH to 1 of the ore. Experience shows that a proportion of 4 to 1 is amply sufficient for fusions for analytical purposes, but for fusions on a commercial scale a proportion of 6 to 7 parts to 1 of the ore is needed. The average time for conducting the fusion is about 2 to 2½ hours at a temperature sufficient to give a clear liquid fusion. It is best to melt the caustic soda first and then slowly to sift in the finely pulverized ore (200-mesh. This, as in the bisulphate fusion, cuts down the frothing.

The use of caustic carbonate (soda ash) requires a high temperature and is hardly more efficient. The proportions used also range from 4 to 8 parts Na_2CO_3 to 1 of the ore.

A mixture of caustic soda and soda ash is a good fusion mixture and does not require as high a temperature as the carbonate.

Caustic soda or caustic carbonate, with additions of sodium fluoride or sodium peroxide, is not much used commercially, as the mixtures offer no particular advantage over the caustic-soda or soda-ash fusions. In analytical work it is said that the addition of sodium fluoride and of peroxide tends to facilitate the breaking up of the silicate ore. In commercial work, however, the breaking up of the silicate ore by NaF or Na_2O_2 is not mandatory and, under proper conditions, can be accomplished by taking a little longer time with other fusion agents.

In caustic fusions the silica is mostly changed to sodium silicate, the zirconium and titanium to sodium zirconate and sodium titanate, and the iron to the hydroxide. An appreciable amount of silica, however, is present as a double sodium-zirconium silicate. The caustic fusions when cooled or leached with H_2O , about 10 liters being used for every kilo of roast. On washing the sodium zirconate tends to be converted into the hydroxide, which is very finely divided and difficult to filter. This difficulty in filtration can be obviated by allowing the leaching liquors to stand for 5 to 6 hours, and then siphoning off the concentrated caustic-soda solution, replacing it with hot water. The washings should not require more than three additions of water to complete the decomposition of the roast if the latter has been well broken up before leaching.

The insoluble residues from the leachings consist of zirconium, titanium, and iron hydroxides, together with some sodium-zirconium silicate. These, with the exception of silica, are now in a form readily soluble in acids, from which the purified zirconium salts may be obtained.

FUSION WITH SODIUM OR POTASSIUM ACID FLUORIDES.

Marignac²⁴³ has suggested that sodium or potassium acid fluorides be used in decomposing zircon and baddeleyite. The general method of procedure is to mix the finely pulverized material with 4 to 6 times its weight of the acid fluoride and gently heat until the moisture is all driven off. The temperature is then raised until the whole mass is fused. The fusion is cooled and boiled with water containing hydrofluoric acid and the insoluble potassium (or Na) silicofluoride filtered off. On cooling the hot filtrate, crystals of potassium (or Na) zirconium fluoride are deposited which can be recrystallized from water.

PREPARATION OF ZIRCONIUM CARBIDE IN AN ELECTRIC FURNACE.

Troost⁴²³ and Moissan²⁴⁹ have prepared the crude zirconium carbide by heating an intimate mixture of zircon and carbon in the electric furnace. The carbide can be treated in various ways but usually is heated in chlorine and the resulting chloride is dissolved in HCl (concentrated); the crystalline oxychloride which separates from this solution on cooling is redissolved and the $\text{Zr}(\text{OH})_4$ precipitated by NH_4OH . The crystallization of the oxychloride will be taken up in detail under Purification of Zirconium Salts in Chapter X.

FUSION WITH CALCIUM OXIDE AND CARBON.

A mixture of zircon⁴²³, calcium oxide, and carbon is heated in the electric furnace (1.030 amperes, 50 volts) for seven minutes. The product, when extracted with H_2O and dilute HCl, is decomposed by Cl_2 at 300°C ., yielding ZrCl_4 .

TREATMENT AFTER FUSION.

Zirconium salts are very hard to obtain pure, directly from the ore, because of the great difficulty in making a complete separation of the zirconium from the associated aluminum, titanium, iron, and silica. Titanium and zirconium are closely allied in their chemical behavior, and only a few reactions afford a clean separation of one from the other.

As the niter cake and the caustic soda fusions are used most frequently on a commercial scale, the general methods of treatment of the fused mass thus obtained are given below. The methods of crystallization, for the production of pure salts, are given in the succeeding chapter.

TREATMENT OF SULPHATE, PYROSULPHATE, ACID SULPHATE, OR NITER CAKE FUSION.

The sulphate solution of the leached fused mass is filtered to remove most of the silica, as stated above, and the solution is then treated in one of the ways described below.

Prolonged boiling precipitates the Zr and Ti from very weakly acid solution as a very voluminous, semicolloidal basic sulphate, which can be repeatedly boiled with dilute 1 to 2 per cent sulphuric acid solution, and decanted practically free from iron but still retaining some of the silica. The precipitated basic sulphates, when treated with NH_4OH while wet, are converted to a hydrated compound that can be filtered from soluble sulphates of sodium and potassium. This precipitate, when dried at 100°C. for some time or baked on a water bath for several hours, can be dissolved in concentrated acids (HCl or H_2SO_4) and the last traces of silica removed. The solution thus formed can be treated by one of the methods given later for the separation of Zr from Ti, and traces of Fe.

The hydroxides of Zr, Ti, Fe, and Al can be precipitated with NH_4OH , washed free of most of the sulphates of sodium or potassium, and the precipitated hydroxides dried at 100°C. , or on the water bath for several hours to dehydrate the silica. Such hydroxides, however, are difficult to filter, and when present in a large quantity practically can not be washed thoroughly. An optional method is first to precipitate with ammonia and then dissolve the freshly precipitated hydroxides in concentrated HCl or H_2SO_4 , evaporating to dryness several times in order to dehydrate the silica. The solution thus obtained is used for the recovery of pure zirconium salts.

The zirconium in the solution can be precipitated as phosphate. A description of this phosphate precipitation is given later.

TREATMENT OF CAUSTIC FUSIONS.

It might be expected that leaching the caustic soda fusion with water would remove the silica. There is no caustic fusion on a commercial scale, however, that entirely eliminates the silica, because of the formation of the double sodium-zirconium silicate. Loveman²³⁹ has patented a process in which, with a fusion of 8 parts Na_2CO_3 to 1 of ore (finely pulverized) over a period of two hours, the silica, on leaching, is claimed to be entirely removed, and the subsequent treatment of this leached roast by digestion in 1:1 HCl solution leaves a hydrated oxide of zirconium with impurities of 0.15 per cent SiO_2 , 0.20 per cent TiO_2 , and 0.10 per cent Fe_2O_3 , giving, it is stated, a 99.55 per cent ZrO_2 .

Loveman's method is a new departure from the general mode of procedure, which usually is to digest in acids the residue from the

leached roast after extraction with water, the acid being either concentrated or dilute, filtering free of insoluble material, and evaporating to dryness on the water bath several times to dehydrate the silica. The mode of procedure from this point depends on the acid used in the digestion of the roast. If HCl is used, the oxy-chloride crystallization may be employed to obtain the chemically pure zirconium salt. If sulphuric acid is used, a crystallization of basic sulphates can be effected, as described further on, or the phosphate precipitation can be employed. If nitric acid is used, a separation similar to that described in the preparation of the nitrate of zirconium may be employed.

CHAPTER III.—PURIFICATION OF THE CHIEF ZIRCONIUM COMPOUNDS.

Zirconium oxide is the principal compound of zirconium that is marketed, partly because of its stability and the ease with which it may be handled, and partly because it has much commercial use at present. The compounds of zirconium and the halogens $\text{ZrF}_2 \cdot 3\text{H}_2\text{O}$, ZrCl_4 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, ZrBr_4 , $\text{ZrOBr}_2 \cdot 8\text{H}_2\text{O}$, ZrI_4 , and $\text{ZrOI}_2 \cdot 8\text{H}_2\text{O}$, etc., are all more or less unstable and readily undergo hydrolysis in dilute aqueous solutions. With the exception of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, these salts are too expensive for ordinary commercial uses and the oxychloride, if prepared, is always ignited to the oxide before being marketed.

The same is true of the sulphates of which there are several varieties, the neutral sulphate, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, zirconyl sulphate, $\text{ZrO}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, basic sulphates, $4\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 14\text{H}_2\text{O}$, $2\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 5\text{H}_2\text{O}$, etc.

Several methods have been suggested in the literature or have been patented for the purification of zirconium compounds, but all based on the characteristic separations of Zr from Ti and other elements in solution. The methods are as follows:

(a) Crystallization of oxychloride. The oxychloride is described by numerous authors as Berzelius¹⁵⁴, Hermann²¹², Venable and Baskerville³⁰⁵, etc.

(b) Preparation of the oxide from fluoride fusions or HF digestion. Marignac²⁴⁸.

(c) Crystallization of basic sulphates (several different varieties). Paykull^{259, 260}, Warren³¹⁰, Hauser²⁰⁰, etc.

(d) Precipitation of phosphate or pyrophosphate. Knop²²⁶, Hautefeuille and Margottet²⁰⁶, etc.

(e) Precipitation with sodium thiosulphate. Loveman^{239a}.

(f) Selective action of HCl , H_2SO_4 (dilute) on the hydrated oxides of Zr, Ti, and Fe. Loveman²³⁹.

(g) Preparation of zirconium nitrate, tannate, pyrophosphate, zirconium carbide and zirconium silicide.

(h) Preparation of miscellaneous compounds of zirconium not discussed in this bulletin.

OXYCHLORIDE CRYSTALLIZATION.

The oxychloride, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, is crystallized from concentrated hydrochloric acid solution. The solubility of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in concentrated HCl at about 15°C . is 10 grams a liter; on warming the

HCl, the solubility of the oxychloride rapidly increases, but on cooling the salt is recrystallized unchanged. The crystals are prismatic needles and belong to the tetragonal system.

In order to prepare this salt, an aqueous HCl solution of Ti and Fe, silica free, is first prepared and evaporated nearly to dryness on the water bath. The crystalline mass that separates out on cooling is redissolved in hot concentrated HCl, and allowed to cool. After standing for 24 to 48 hours, the crystals are filtered free of mother liquor and washed thoroughly with cold concentrated HCl. Several such crystallizations are required to obtain pure $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$.

As the amount of iron, sodium, aluminum, and other salts present has much effect in retarding this method of purification, the number of recrystallizations and details of treatment are varied somewhat for material prepared from different ores and by different methods of ore fusion. For successful operation it is necessary to obtain first, prior to crystallization, a concentrated HCl solution of the chloride in which the water present is reduced to the minimum.

PREPARATION OF THE OXIDE FROM FLUORIDE SOLUTIONS.

The oxide of zirconium, ZrO_2 , may be prepared from the fluoride (ZrF_4), the double potassium salt (K_2ZrF_6), the double ammonium salt ($(\text{NH}_4)_2\text{ZrF}_6$), or the double sodium salt (Na_2ZrF_6).

The potassium fluozirconate is the most important of the double fluorides. As has been stated, it is readily obtained by digesting zirkite with hydrofluoric acid, diluting and filtering the zirconium fluoride solution, and precipitating the double salt from the hot aqueous solution by the addition of potassium fluoride, potassium hydroxide, or potassium chloride. It may also be obtained by fusing zircon with acid potassium fluoride, digesting the fused mass with boiling H_2O plus HF, filtering free from the potassium silico-fluoride while hot, and crystallizing the salt from the filtrate.

The double potassium fluozirconate crystallizes from these solutions in small rhombic prisms, and is dissolved in boiling water from which it is recrystallized on cooling. Its solubility in water has been estimated as being 1.41 parts K_2ZrF_6 in 100 parts of water at 15°C ., and 25 parts K_2ZrF_6 in 100 parts of water at 100°C . By repeated recrystallization, the K_2ZrF_6 is obtained free from all impurities.

The salt $\text{K}_2\text{ZrF}_6 \cdot \text{KF}$ is prepared by dissolving zirconium hydroxide in the smallest quantity of hydrofluoric acid and then pouring the liquid into a concentrated solution of neutral potassium fluoride. The salt is recrystallized from boiling water in the form of fine needles.

K_2ZrF_6 is obtained by adding a large excess of KF to a zirconium fluoride solution.

$\text{KZrF}_5 \cdot \text{H}_2\text{O}$ is obtained by adding a large excess of zirconium fluoride to a solution of potassium fluoride.

Sodium-zirconium double fluorides are obtained in the same manner as the potassium salts and are recrystallized from hot aqueous solutions in the same way. These salts, however, are much less soluble in water than the potassium salts and are much harder to purify. Because of their low solubility they may be obtained by double decomposition of the potassium salt with sodium chloride. If sodium fluoride and zirconium fluoride are mixed in any proportion the salt $\text{Na}_2\text{ZrF}_6 \cdot 3\text{NaF}$ is produced; it separates from hot aqueous solutions in the form of small monoclinic crystals. One part of this salt is soluble in 258 parts of water at 18°C . and in 60 parts of water at 100°C .

The ammonium double fluorides are analogous to K_2ZrF_6 , and, although more soluble in water, their recrystallization is effected in the same manner.

Other double fluorides are known that have the general formula $\text{R}_2\text{ZrF}_6 \propto \text{H}_2\text{O}$, or $\text{ZrF}_4 \cdot 2\text{RF} \propto \text{H}_2\text{O}$ and $\text{ZrF}_4 \propto \text{RF} \propto \text{H}_2\text{O}$.

In order to obtain the oxide from the double fluorides (except the ammonium salt) the latter are digested with H_2SO_4 and carried down to fumes of SO_3 . The soluble sulphates formed are dissolved in water; the zirconium is precipitated with ammonia and washed free of sulphates; and the hydroxides are ignited at a dull red heat to the oxide. The ammonium salt can be ignited directly to the oxide at ordinary pressures.

ZIRCONIUM SULPHATES AND BASIC SULPHATE CRYSTALLIZATIONS.

Zirconium in sulphate solution forms a variety of complex compounds and zirconyl radicals which seem to be dependent on the temperature and concentration of the solution. Basic sulphates are easily crystallized or precipitated out from sulphate solutions, some by boiling under pressure, some by simple boiling of a very dilute solution, and some by maintaining a solution of certain concentration of zirconium or of sulphuric acid at a certain temperature, which variance of temperature (from 20°C . to 250°C . (under pressure)) will yield various basic salts of varying compositions. Zirconium sulphate solutions are prepared by:

1. Digesting the oxide or mineral in HF , adding H_2SO_4 and evaporating to fumes of SO_3 . The sulphates formed are soluble in water or dilute H_2SO_4 .

2. Digesting the caustic soda fusion in H_2O and dissolving the precipitated hydroxides in H_2SO_4 of sufficient concentration, and evaporating to fumes of H_2SO_4 .

3. Digesting of the oxide which has not been highly ignited in hot concentrated H_2SO_4 .

4. Fusing the mineral or oxide with niter cake, pyrosulphates, or acid sulphates, and subsequently leaching with sulphuric acid or water.

The basic sulphates of zirconium offer possibilities for good commercial methods for separating Zr from Ti and Fe. Some of the basic salts, however, are analogous to the Ti compounds, and for these the separation is tedious.

One fact regarding the sulphate crystallization which has found commercial use is that when $\text{Zr}(\text{SO}_4)_2$ is dissolved in H_2SO_4 plus H_2O , the solubility of the salt in strong acid increases with the increased concentration of the SO_3 . When a solution containing 61 per cent SO_3 is obtained, $\text{Zr}(\text{SO}_4)_2$ has a maximum solubility and, on standing, an acid sulphate ($\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$) crystallizes out. The crystallization is usually complete in 4 to 12 days when maintained at a temperature of 39 to 40° C.

A second method is mentioned in the United States patent of Askenasy:¹⁴²

A dilute solution of zirconium in HCl , H_2SO_4 , or a mixture of the two, containing impurities of iron, with not more than 9 per cent $\text{Zr}(\text{OH})_4$, is heated in an autoclave for 5 hours to a temperature of 200° C. The zirconium is changed to an oxyhydrate and is obtained in a form easily filterable, and on igniting yields a perfectly white product.

A third method mentioned is to boil a very concentrated solution of the sulphates of Zr, Ti, and Fe. If the solution is kept at the boiling point for some time and then gradually cooled, a basic salt having the formula $2\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 5\text{H}_2\text{O}$, separates out. This salt has a density of 2.834 and is slightly soluble in H_2O to an acid reaction. When a very dilute solution is boiled, no separation of this salt occurs. An abstract of the recent work of Glazebrook, Rosenbain, and Rodd^{187a}, which refers to the basic sulphate and oxychloride methods of separation is appended:

Basic Zr sulphate is obtained by the addition of an alkali, such as ammonia or caustic soda, to an acid solution containing Zr sulphate, and preferably HCl until a faint precipitate begins to form, and then allowing the precipitation to continue by itself. The sulphate solution can be made by heating together the crude ZrO_2 , CaF_2 and H_2SO_4 , adding water, separating the CaSO_4 and adding some HCl . The basic sulphate can be converted to the oxide by ignition, or to the hydroxide by suspending in water and agitating with ammonia. The basic sulphate can be made in more pure condition by dissolving the hydroxide in HCl and crystallizing a new basic Zr oxychloride, $\text{Zr}_2\text{O}_3 \cdot \text{Cl}_4 \cdot 22\text{H}_2\text{O}$, with the known $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ being obtained. The new oxychloride is separated by recrystallization from HCl and is dissolved in water and treated with H_2SO_4 or a sulphate equivalent to the contained Cl , the new basic sulphate $5\text{ZrO}_2 \cdot 2\text{SO}_3 \cdot 14\text{H}_2\text{O}$ being precipitated. The HCl mother liquor contains Zr which may be precipitated as a basic sulphate free from Fe by addition of H_2SO_4 .

Other methods have been mentioned in the literature but the descriptions are not complete. In some of the sulphate crystallizations it is found that Ti also crystallizes out with the Zr. For use in the enameling industry, for paints and lacquers this does not prove a detriment in the finished product.

ZIRCONIUM PHOSPHATE PRECIPITATION.

Precipitation of zirconium phosphate affords a good analytical means of estimating zirconium. It is the only phosphate which will be precipitated from dilute acids in the presence of hydrogen peroxide (3 to 20 per cent H_2SO_4). Hillebrand^{366a} utilizes this property in determining zirconium in minerals, and claims it is sensitive to very small percentages of ZrO_2 in the sample. Zirconium phosphate has a variable composition, although it is usually estimated, for small percentages in rocks and minerals, to contain approximately 50 per cent ZrO_2 . For delicate and accurate results, the phosphate, after being thoroughly washed, is fused with caustic soda and the leached residue is ignited to the oxide.

When any of the compounds of zirconium are dissolved in concentrated H_2SO_4 , the solution diluted to about 10 per cent acid, a little H_2O_2 or Na_2O_2 added and any soluble phosphate added to the solution, the zirconium is precipitated as the phosphate, practically free of Ti and many other impurities.

The application of the phosphate in commercial work is made by Carney¹⁶². Although primarily intended for the separation of thorium from other rare earths, their method is adaptable to zirconium ores that contain no thorium.

In all of the mentioned methods of obtaining practically pure salts of Zr from the ores, as has been stated, the oxide is obtained either by direct ignition of these products or by digestion in acids, precipitation with ammonia, and subsequent ignition. In the phosphate precipitation method the ignited phosphate is fused with caustic carbonate, leached with water, digested with 1:1 HCl, or H_2SO_4 , and the well-washed residue is ignited to the oxide. An optional method is to dissolve the still wet phosphate (which has been washed thoroughly with 2 per cent H_2SO_4 plus H_2O_2) in hot concentrated H_2SO_4 , cool, dilute, and nearly neutralize with Na_2CO_3 . The solution then is precipitated with sodium thiosulphate and the washed hydroxides ignited to a dull red heat.

PRECIPITATION OF ZIRCONIUM WITH SODIUM THIOSULPHATE.

Loveman^{239a} claims that if a sulphuric acid solution of zirconium sulphate containing impurities of iron and aluminum is diluted until there is 1 part of acid to 6 parts of water and sodium thiosulphate

is then added, either solid or in solution, the zirconium precipitates as $\text{ZrO}_2\cdot\text{H}_2\text{O}$. After agitation and heating with steam the precipitate is filtered, dried, and ignited to ZrO_2 . It is stated that the iron and aluminum stay in the solution.

SELECTIVE ACTION OF HYDROCHLORIC ACID, SULPHURIC ACID, (DILUTE) ON THE HYDRATED OXIDE OF ZIRCONIUM, TITANIUM, AND IRON.

This method of Loveman's²³⁹ has already been mentioned at the end of Chapter II under "Treatment of caustic fusions." As has been stated, Loveman claims that the hydroxides of iron and titanium are more soluble in dilute mineral acids than the hydroxide or hydrated oxide of zirconium; and that these impurities can be dissolved out of the residue left from the soda ash fusion. This method, as well as most of the others, is discussed later.

OTHER SALTS OF ZIRCONIUM.

ZIRCONIUM NITRATE.

Only a few other salts of zirconium are prepared on a commercial scale. The most common of these is the nitrate, which is made by dissolving the freshly prepared oxide in nitric acid and evaporating in a desiccator over sulphuric acid or sodium hydroxide.

The zirconium separates as a gummy-white substance, believed to be a zirconylnitric acid of the composition $\text{ZrO}(\text{NO}_3)_2\cdot 2\text{HNO}_3\cdot 4\text{H}_2\text{O}$. When this salt is dissolved in water and the aqueous solutions are warmed, various basic salts separate out.

A second method consists in dissolving the freshly precipitated hydroxide of zirconium in concentrated HNO_3 , but with no considerable excess of acid. The presence of a small quantity of ammonium sulphate in a solution of zirconium nitrate causes the separation of the salt when the solution is boiled and allowed to cool. An excess of $(\text{NH}_4)_2\text{SO}_4$ will dissolve this material.

This salt is insoluble in H_2O , but soluble in HNO_3 , and when digested with NH_4OH is converted to zirconium hydroxide, which can be dissolved in HNO_3 and evaporated on a water bath to a clear gumlike crust of zirconium nitrate (or zirconylnitrate).

This method is particularly adapted for use in the manufacture of incandescent light mantles, for making zirconium nitrate from impure oxide or from the ore directly, as the precipitation in the presence of $(\text{NH}_4)_2\text{SO}_4$ of the zirconium in a nitric acid solution is complete and is entirely free of Ti and Fe. Iron is an impurity that is detrimental in an incandescent body.

ZIRCONIUM TANNATE.

Zirconium tannate is mentioned as being valuable in the arts and in industry and as an antiseptic. It is prepared by dissolving the neutral sulphate of zirconium in boiling water so as to obtain a solution containing 10 parts by weight of salt to 90 parts of water. To this solution is added a saturated solution of tannic acid, slowly, until there is no further precipitation. This is filtered and the precipitate thoroughly washed with boiling water and dried.

It is insoluble in cold or hot water, alcohol, ether, fatty or aromatic oils, hydrocarbons, etc., has no taste or odor, and is nonpoisonous.

ZIRCONIUM HYPOPHOSPHITE.

One of the most interesting of the zirconium compounds, according to Herzfield,²⁰⁴ is the hypophosphite, which is sensitive to light. It is prepared by adding hypophosphorous acid to a nitrate solution of zirconium. A precipitate is obtained that redissolves in an excess of the acid; on the addition of alcohol to the solution, crystals (colorless, highly refractive prisms) of the formula $\text{Zr}(\text{H}_2\text{PO}_2)_4 \cdot \text{H}_2\text{O}$ are thrown down. On exposure to direct sunlight, these crystals rapidly become violet.

ZIRCONIUM CARBIDE.

Zirconium carbide (Moissan²⁴⁹, Wedekind³¹³) is readily formed by ignition of zircon, zirconia, or any other compound of zirconium with carbon. It is a gray-black solid; after fusing it is hard enough to scratch glass. It is used as the starting point in many methods of purifying zirconium minerals, as it is readily acted on by oxygen or the halogens. The heating together of CaCO_3 , C, and zircon is said to give a good grade of carbide after extraction with dilute hydrochloric acid.

ZIRCONIUM SILICIDE.

Zirconium silicide (ZrSi_2) (Honigschmidt²¹⁹) may find some metallurgical uses as zirconium is introduced into iron or steel most easily as the silicide. It is prepared by the alumino-thermic process (200 parts Al, 250 parts sulphur, 180 parts sand, and 40 parts K_2ZrF_6 , covered with a thin layer of magnesium as a priming agent). Zirconium silicide is not attacked by acids, except hydrofluoric, and is decomposed only slowly by caustic potash.

MISCELLANEOUS COMPOUNDS OF ZIRCONIUM NOT DISCUSSED IN THIS BULLETIN.

Numerous salts listed in the textbooks have no commercial uses at the present time, and consequently have not been used in this investigation. Among these salts are the basic carbonate $\text{ZrCO}_3 \cdot \text{ZrO}_2 \cdot 2\text{H}_2\text{O}$, and $\text{ZrCO}_3 \cdot \text{ZrO}_2 \cdot 8\text{H}_2\text{O}$, the zirconyl oxalates $\text{ZrOC}_6\text{O}_4 \cdot \text{ZrOH}(\text{HC}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$, the tartrate $\text{ZrO}(\text{C}_4\text{H}_4\text{O}_6\text{K})_2 \cdot 3\text{H}_2\text{O}$ and various compounds with organic precipitants.

CHAPTER IV.—TECHNICAL USES OF ZIRCONIUM COMPOUNDS.

Of the compounds of zirconium that have found technical application, the oxide (ZrO_2) is the most important. Zirconia exists in two forms—amorphous and crystalline. The amorphous is a white powder of flourlike appearance when finely pulverized, and exceedingly inert toward chemical agents. This inertness increases with the temperature to which it has been ignited. The density has been variously given as 4.3 (Berzelius,¹⁵³) and 5.85 (Nilson and Pettersson²⁵⁴). Angstrom¹³⁸ estimated the specific heat as being 0.1076. Until recently the melting point has not been given, although it was known that zirconia volatilized at the temperature of the electric arc. Linnemann²³⁷ and others studied the spectrum in the oxyhydrogen flame. Angstrom states that zirconia is diamagnetic.

Crystalline zirconia, according to Nordenskjöld²⁵⁵, has a density of 5.742 at 15° C. Troost and Ouyard³⁹⁵ estimated the density as 5.726 at 17° C.; Knop²²⁵ as 5.42. Levy, and Bourgeois³⁷³ give the density of hexagonal crystals as 4.9.

Zirconia, as prepared in the laboratory or by commercial methods from the ore, is usually amorphous. It can, however, be fused in the electric arc furnace. The physical properties of hexagonal crystals of ZrO_2 are summed up in Table 2. Some of these values can not be considered better than approximations.

TABLE 2.—*Properties of fused zirconia.*

Specific gravity.....	5.74 (²⁵⁵)
Melting point.....	2,500° C. (^{256a})
Boiling point.....	4,300° C. (²⁵⁶)
Specific heat (amorphous).....	0.1075 (²⁵⁴)
Coefficient of expansion (fused zirconia, about the same as fused quartz).....	0.0000084 (²⁵⁴)
Heat conductivity (about the same as fused quartz).....	Very low
Electrical resistance.....	(1,200° C.) 1.2×10^3 ohms per cm. ³ (^{172d})

Zirconia is highly resistant to most acids with the exception of hot concentrated H_2SO_4 and HF after ignition to a relatively low temperature. When ignited to higher than 2,000° C., or even fused, resistance to the action of acids increases until the fused zirconia is decomposed by HF only, and then very slowly. The resistivity to

the action of caustic, bisulphate, or acid fluoride fusions also increases with the degree of calcination, and fused zirconia is attacked slowly.

USE OF ZIRCONIA AS A REFRACTORY.

A number of articles and patents relate to the use of zirconia for refractory purposes. Crude baddeleyite possesses some of the properties of pure zirconia, but the impurities in the crude oxide lower the melting point considerably. Table 3 gives the melting point of pure ZrO_2 as $2,950^\circ \text{C}$., but it is estimated that 0.5 per cent impurities lower the melting point 100°C . Stansfield^a gives the melting point of other refractory materials as follows:

TABLE 3.—*Melting points of refractories.*

Substance.	$^\circ \text{C}$.
Magnesia (pure)-----	2,800
Zirconia-----	2,500-2,950
Lime (pure)-----	2,570
Carborundum-----	2,200
Alumina (pure)-----	2,050
Silica-----	1,700

USE OF UNFUSED ZIRCONIA.

Zirconia not previously ignited to a very high temperature can not be used successfully for the manufacture of refractory ware, such as dishes and tubes, the difficulty being that no suitable binders are known that will not lower the melting point too much. Also, the ordinary unfused zirconia shrinks on heating, so that cracks develop in ware prepared from it.

USE OF FUSED ZIRCONIA.

When, however, the dishes are prepared from the fused or nearly fused oxide, much of this difficulty is obviated. It is said that platinum can be melted to a clear mobile liquid in such a dish. Owing to the low coefficient of expansion of fused zirconia, it can be heated red hot and plunged into water without cracking. This property, with the great resistivity of the oxide, after ignition to a very high temperature, to fused alkalis, fused cyanides, and to acids, has caused it to be gradually developed for use in chemical ware.

Much work has been done on the preparation of refractory vessels from zirconia in an attempt to use material that has not been previously fused. The use of other refractories, such as Al_2O_3 , MgO , etc., to make the dishes more impervious, and binders, including

^a Stansfield, Alfred, *The electric furnace; its construction, operation, and uses*. New York, 1914. 415 pp.

clay and starch, to prevent cracking, have been investigated by several authors.

A number of extracts from articles on the subject are appended. Podszus²⁶⁶ says:

If the raw, impure zirconia is used for refractories they crack. If a bond is used to overcome the trouble, refractoriness is reduced. Zirconia heated to above $2,000^{\circ}$ or preferably fused gives no trouble. For fusing, a carbon electrode is buried in coarsely ground, calcined zirconia and an arc is formed with a second carbon electrode, thus partly melting the zirconia. The ZrO_2 acts as an electrode and as the zirconia fuses the upper carbon electrode is gradually withdrawn; fusion is then rapid. Arcs 30 cm. long with molten zirconia 15 cm. in diameter are obtained in one-half hour with a current of 50 amperes at 200 volts. The resulting zirconia is pure and white with some yellowish sheen from Fe impurity. The fused zirconia is ground for 100 hours or longer in a ball mill and washed with acid to remove the Fe introduced. The product may be pressed into shape with or without an organic binder, or it may be cast like clay ware. The articles are burned to $2,300^{\circ}$ to $2,400^{\circ}$ to take out shrinkage, which often amounts to 20 per cent. Burning may be reduced to $2,100^{\circ}$ by the addition of a little B_2O_3 or H_3PO_4 , but this is not to be recommended. Fused zirconia is very difficult to grind, being far more resistant to crushing than cold quartz. It is not harmed by being quenched from redness in cold H_2O . Its hardness is between that of quartz and corundum, specific gravity 5.89, porosity under 1 per cent, and melting point $2,950^{\circ}$ to $3,000^{\circ}$. The presence of 0.5 per cent impurity lowers the melting point about 100° .

Another method for the preparation of zirconium ware is as follows:

In the production of Zr refractories the ZrO_2 is first fused in a modified type of arc furnace at 50 amperes 220 volts, and afterward ground in a steel ball mill. The powder is then molded, or pressed into the required shape with or without a binder. By grinding a portion to 200 mesh it becomes colloidal in the presence of H_2O and can then be used as a plastic cement for binding the material. After gradual heating the articles are burned at $2,300^{\circ}$ to $2,400^{\circ}$ C. until contraction ceases, in a cylindrical oven of the injector type, the fuel being either town gas, petroleum, or acetylene supplied with blast of air and finally with one of oxygen. The crucibles should give a clear ring when tapped and have as fine a texture as porcelain.

Zirconia is pressed into shape in a mold and dried at 120° to 130° C. and then heated very gradually to $1,500^{\circ}$ C. in a gas furnace and maintained for 2 hours at that temperature. It is found that the greatest resistance to high temperature (up to $2,000^{\circ}$ to $2,400^{\circ}$ C.) is given by zirconia obtained by precipitating the hydroxide and igniting at $1,400^{\circ}$ for 10 hours. While natural zirconia containing 83.5 per cent ZrO_2 gives the lowest porosity, crucibles of this material can not be employed above $1,900^{\circ}$ C., as they soften and lose silica by volatilization. They require much less rapid heating than crucibles of purified zirconia. The addition of 1 per cent dry starch when mixing is of advantage, but increases the porosity.

USE OF OTHER REFRACTORIES WITH ZIRCONIA.

The main effect of other refractories mixed with zirconia in the preparation of vessels of this ware is to lower the melting point of the zirconia. Beryllium oxide, alumina, thoria, and yttria are said

to be suitable additions, owing to the close proximity of their melting temperatures and to their small volatilization between $2,000^{\circ}$ and $2,400^{\circ}$ C. Small amounts of beryllium oxide and alumina lower the melting point of zirconia somewhat, but in no case below $2,400^{\circ}$ C. Thoria and yttria hardly lower the melting point at all. A mixture of equal parts zirconia and carborundum, the latter coarser grained, is said to be highly refractory without showing the usual tendency of zirconia to break and lose coherence (Pfaff^{263a}).

It is also claimed that beryllium oxide and magnesia, when used in small quantities, reduce the porosity of zirconia ware. For ware used for temperatures up to $2,000^{\circ}$ C. additions of 1 per cent alumina have been recommended; up to $2,200^{\circ}$ C. about 1 per cent thoria; to $2,400^{\circ}$ C. about 1 to 3 per cent yttria. Larger additions are said to be useless and to increase the porosity. Quartz or platinum can be melted in crucibles containing 10 per cent magnesia without injury to the crucible. Meyer²⁴⁸ has experimented with mixtures of fire clay and zirconia. An excerpt from his article is given below. Although he worked with baddeleyite (95 per cent ZrO_2), the results are of interest in the present discussion.

Meyer says that zirconia bonded with 5 per cent Warrior Ridge fire clay stands the temperature of cone 32 easily. Crude zirconia alone shows a linear shrinkage of 9 per cent when fired to $2,600^{\circ}$ F., and it is claimed that natural zirconia develops very fair plasticity upon wet grinding.

A mixture of 93 per cent ZrO_2 (95 per cent) and 7 per cent dry branch kaolin had a firing linear shrinkage of 12 per cent at $2,600^{\circ}$ F. Sorrel cement, phosphoric acid, and sodium silicate were tried as binder. Water-ground ZrO_2 proved most satisfactory. Fire clay lowers the melting point too far to be satisfactory. Also zirconia has a considerable lower thermal conductivity than magnesite, and quite probably the lowest of any available material that will withstand $1,800^{\circ}$ C. At this temperature ZrO_2 bonded with clay softens somewhat; a brick made from the material can be considered among the highest refractories.

Ruff, Seiferheld, and Bruschke²⁸⁷, Ruff, Otto²⁸⁴, and Ruff and Lauschke^{286a} have published articles on the use of ZrO_2 with other refractory oxides. They claim that ZrO_2 , MgO , and BeO are the only oxides available for the preparation of crucibles for use in a reducing atmosphere at temperature above $2,000^{\circ}$ C., and of these MgO is excluded because of its volatility and BeO because of its cost. Experiments are described in which ZrO_2 was made into crucibles with various binders and the properties of the product determined. The best mixture was found to be ZrO_2 , 97 parts; MgO , 3 parts; with large pieces the addition of 1 part of starch was found advisable. The

latter mixture is dried 1 hour at $1,000^{\circ}$, then 3 hours at $1,400^{\circ}$; both are burned to at least $1,500^{\circ}$ C. The crucibles can be used at temperatures up to $2,200^{\circ}$ C. in a vacuum furnace, though there is some carbide formation. With pure ZrO_2 the shrinkage is about 6.5 per cent; with crude materials it is much greater. Although they were always porous, ZrO_2 crucibles have been used for the preparation of tungsten alloys and for the determination of the boiling point of Fe, Ni, Mn, and Co.

SHAPING OF ZIRCONIA WARES.

In the manufacture of ZrO_2 refractories there are two general methods of shaping the articles to be made from the prepared body of ZrO_2 —pressing and casting.

PRESSING.

Plastic pressing.—In plastic pressing the prepared material is thick enough to be beaten or rolled out into a thin cake or “bat,” which is pressed into molds of plaster of Paris. On standing the article dries a little, frees itself from the sides of the mold, and can be easily removed.

Dry pressing.—In dry pressing the material is dampened just enough so that a handful when squeezed will adhere loosely together. This is filled into a metal mold and a die is forced down on it by a hand or hydraulic press. The article formed is afterwards removed and smoothed up.

CASTING.

Casting is the simplest method and is much used in making pottery wares when the mixtures formed do not yield a very plastic body.

The clay is suspended in water, the mixture having such a consistence that it pours fairly readily—in clays the consistence represents a weight of 1 pint as equal to 30 ounces—and is then poured into molds of plaster of Paris. These molds, being somewhat porous, absorb water from the material, and a coating of the body is deposited on the sides of the mold. When a sufficient thickness of body has been deposited, the excess liquid material is poured out and the mold set away to dry. When dry, the crucible or other object formed, shrinks away from the sides of the mold and can be easily slipped from it.

Recently Mr. C. M. Johnson of the Crucible Steel Co. of America has put on the market an acid-proof refractory ware made, it is said, of zirconia and zirkite. Experimenters who have tried zirkite ware claim that there is much more tendency to cracking and shrinking than has been previously supposed. Johnson, however, claims that this

ware is very refractory and can be used for many purposes for which porcelain is unsuitable.

According to Meyer,⁸⁸

The demand for zirkite bricks was active throughout 1918, increasing toward the closing months. All of the standard brick shapes required by the trade are now available, and the use of this new basic refractory is well past the experimental stage. A standard 9-inch zirkite "straight" weighs approximately 12 pounds and sells in carload lots at prices comparing favorably with magnesite brick, life and efficiency being considered.

During the first quarter of 1918 the demand for this refractory was mainly for furnace lining as well as for other purposes where a refractory having a low coefficient of expansion, high melting point, and maximum resistance to slag corrosion is demanded.

OTHER TECHNICAL APPLICATIONS OF ZIRCONIA AND ZIRCONIUM COMPOUNDS.

Besides its use in refractories, zirconia²⁴⁵ is used in the enamel industry as an opaquing medium. Other compounds of zirconium, such as hydrated silicate, basic zirconium salts containing acid-free radicals, and hydrated alkali-containing compounds of zirconium, are used as clouding agents in enamels.

A typical batch for preparing an opaque iron enamel is given as follows:

Batch for an opaque iron enamel.

	Per cent.
Feldspar -----	37.0
Borax -----	18.0
Quartz -----	21.0
KNO ₃ -----	7.0
ZrO ₂ -----	8.0
	100.0

Although the oxide has not proved satisfactory for gas mantles, amounts higher than 1 per cent decreasing the emissivity of a mantle, nor for arc lamps, it has been used for polishing powders, insulators for both heat and electricity, and with fair success in the Nernst lamp. Some zirconia is also used as a substitute for calcium oxide in the Drummonds light. Being absolutely nontoxic ZrO₂ is finding a use in paints and lacquers, where its resistivity to physical and chemical agents is proving highly valuable. The soft white powder has good covering power and makes a good pigment.

As an abrasive zirconia, zirconium silicide, and zirconium carbide are suggested for a variety of uses, the carbide particularly as a substitute for the diamond in cutting glass.

The use of zirconium salts have been tried for mordants. Wengraf³³² tested the statements of Liebermann²³⁶ that zirconium salts

make stronger mordants than aluminum, chromium, or iron salts, and found that in certain cases the zirconium salts gave more intense colors than corresponding amounts of aluminum salts.

As ZrO_2 is nontoxic, it is used in place of bismuth, nitrate, or carbonate in Röntgen-therapy. It is also said to have some medicinal value.

Zirconium oxide and nitride have been suggested for use in the extraction of oxygen and nitrogen from the air. There have also been statements to the effect that the oxide may find use as a filler in the manufacture of rubber goods.

CHAPTER V.—ANALYTICAL DETERMINATION OF ZIRCONIUM IN METALS AND ORES.

W. F. Hillebrand^{366a} has suggested a method based on the procedure previously suggested by G. H. Bailey³³⁸ which works well for the determination of small amounts of zirconium in minerals. The mineral is fused with sodium carbonate containing a little potassium nitrate; the fused mass is cooled, disintegrated with water, and the residue is washed with a dilute solution of sodium carbonate. Then the residue is treated with dilute sulphuric acid and the barium sulphate or other insoluble material removed. To the solution which does not contain more than 1 per cent H_2SO_4 and a little hydrogen peroxide a few drops of a solution of an orthophosphate are added and the zirconium comes down as a flocculent precipitate of zirconium phosphate or basic phosphate. The precipitate is collected on the filter, ignited, fused with a little potassium acid sulphate, brought into solution with a little dilute H_2SO_4 , and the zirconium phosphate again precipitated. The zirconium is weighed as the phosphate, which by theory should be 51.8 per cent ZrO_2 . If the amount is large the residue is again brought into solution by suitable fusion and the hydroxide precipitated with ammonia and the zirconium weighed as the oxide.

It can be said of the above procedure that the phosphate precipitation could be made quantitatively in a much stronger sulphuric acid solution. If there is considerable iron and titanium in a 1 per cent H_2SO_4 solution, the zirconium phosphate will be impure. If the solution contains as much as 5 per cent H_2SO_4 , together with a little H_2O_2 , the precipitate will be nearly free from both iron and titanium. Some later authors, like Schiotz³⁸⁵, recommend precipitation of zirconium phosphate from 10 per cent sulphuric acid solution. Nicolar-dot and Reglade^{376a} recommend the use of a 20 per cent H_2SO_4 solution for the precipitation of zirconium phosphate. Biltz and Mecklenburg³⁴¹ have found that zirconium is the only substance known which is precipitated by Na_2HPO_4 from dilute hydrochloride acid solutions.

A number of different methods of procedure have been suggested for separating zirconium from other elements. Streit and Franz^{385b} boil the neutralized solution of sulphates with a 50 per cent excess of acetic acid, which precipitates the zirconium. This procedure, however, does not separate the iron from the zirconium. Bailey precipitated the zirconium as ZrO_3 or Zr_2O_5 with strong hydrogen peroxide solution, but Davis³⁴⁸ separated Al and Zr by precipitating the zirconium with sodium iodate from a feebly acid solution. The acid must be very dilute and if there is much titanium, the separa-

tion is not all that might be desired. Baskerville³⁴⁰ suggests the precipitation of zirconium and titanium from a neutral solution with sulphur dioxide or sodium thiosulphate, but Walker³⁸⁹ separates zirconium from uranium by the peroxide method.

Iron and zirconium have been separated by dissolving the FeCl_3 from the mixed chlorides in a dry ether solution of HCl ; but Havens and Way³⁶² separate Fe from Cr, Zr, and Be by passing HCl over the oxides. Gutbier and Hüller³⁵⁸ claim to make a quantitative separation of iron and zirconium by precipitating together as hydroxides and igniting: on reduction with hydrogen the iron is reduced to the metal, but the ZrO_2 is unchanged. The peroxide method was revived by Geisow and Horkheimer³⁵⁷. Knorre³⁷⁰ separated iron from zirconium and other metals by precipitating with nitrosobetanaphthol. Hartwell³⁶¹ found that certain general separations could be made of Ce, La, Nd, Pr, Th, and Zr by use of the chlor anilines and beta methylene tetramine. Dittrich and Pohl³⁵¹ estimated Ti and Zr in rocks by weighing the two together and estimating the Ti colorimetrically, the Zr being found by difference. Dittrich and Freund³⁵⁰ tried the separation of zirconium from Ti, Fe, and Th by the ammonium salicylate and the sodium acetate methods. Wunder and Jeanneret³⁹⁴ used the method for the precipitation of zirconium as a phosphate. Ferrari³⁵⁵ suggested the use of cupferron (ammonium phenylnitrosohydroxylamine) in acid solutions for the quantitative precipitation of zirconium. Later Brown³⁴³ tried the separation of Zr, Ti, and Fe from Al and Mn with the same reagent.

Headden³⁶⁴ published a paper on the estimation and separation of the fluorides of titanium, columbium, tantalum, and zirconium. Kelley and Myers³⁶⁹ suggested a method for the analysis of alloys of nickel and zirconium, and Ferguson³⁵⁴ gave a method for the analysis of ferrozirconium and zirconium in steel. Thompson^{386a} gave a method of analysis that in most respects is similar to some of the methods already mentioned. Recently Johnson^{368a} has published an article on the "Determination of uranium, zirconium, chromium, vanadium, and aluminum in steel."

Abstracts of some of the recently published methods of determining zirconium follow. They will give an idea of the most popular methods used at present. In some of them, at least, there is still much to be desired as regards simplicity and accuracy.

ANALYSIS OF FERROZIRCONIUM AND ZIRCONIUM IN STEEL.

J. D. Ferguson³⁵⁴ says:

Dissolve in a 250-c. c. beaker 1 gram of Fe-Zr in 25 c. c. of a mixture of 100 c. c. of H_2O plus 50 c. c. concentrated HCl ; with Zr steel use 3 grams and 50 c. c. of the acid mixture. Evaporate to dryness and absence of white fumes,

cool, add 30 c. c. of hot H_2O , then 1 c. c. of concentrated H_2SO_4 , and heat till all soluble salts dissolve. Filter by suction, wash the SiO_2 several times with boiling H_2O , then with a boiling mixture of 1 c. c. concentrated H_2SO_4 plus 20 c. c. H_2O , pouring it dropwise around the edge of the filter; then wash again several times with boiling H_2O . The purpose of this is to have only the necessary amount of H_2SO_4 present in solution, if more acid is used, a careful neutralization must be performed afterwards. Save the filtrate. Ignite the residue and paper in a platinum crucible (if the SiO_2 is dark gray, insoluble Zr silicide may be present). weigh, add 3 c. c. concentrated H_2SO_4 and 3 c. c. of HF , evaporate till SO_3 fumes are evolved; cool, add 3 c. c. of HF and evaporate (repeat if necessary to insure the complete removal of SiO_2). Finally evaporate to dryness. If any appreciable residue remains, fuse for 30 minutes with a large excess of Na_2CO_3 ; dissolve the melt in hot H_2O , filter off any insoluble Na_2ZrO_4 , Fe_2O_3 , etc., ignite, and fuse thoroughly with $\text{K}_2\text{S}_2\text{O}_7$.

Dissolve this melt in hot H_2O and add to the filtrate from the SiO_2 , dilute to 400 c. c., heat to boiling, then add slowly and with constant stirring a boiling solution of $\text{Na}_2\text{S}_2\text{O}_3$ (dissolving 6 grams for each gram of alloy taken in the smallest amount of H_2O necessary). The liquid becomes almost colorless; a little precipitated sulphur does no harm, but avoid precipitating a large excess. Now add, while stirring well, a boiling solution of 1 gram of Na_2HPO_4 dissolved in a little H_2O (if any appreciable quantity of Zr is present, it precipitates almost immediately as a whitish or greenish flocculent precipitate); boil for a few minutes, let stand about 30 minutes, filter through a 15 cm. paper without suction, decanting carefully at first. Wash about ten times with hot H_2O , stirring the precipitate up thoroughly by directing a forcible jet against the sides of the filter. Dry the filter, burn the precipitate and paper separately, and weigh as Zr phosphate ($\times 0.3828 = \text{Zr}$).

NOTES.—(1) The Fe must be reduced to Fe^{2+} condition. (2) The solution before precipitation must be approximately 1 per cent acid (H_2SO_4), to prevent Fe and Al from precipitating. (3) A pinkish color to the freshly precipitated Zr phosphate indicates the presence of Ti. The precipitate containing Ti is washed, dried, and ignited as usual, fused with at least thirty times its weight of Na_2CO_3 for 0.5 to 1 hour, the melt dissolved in H_2O , and the insoluble Na_2ZrO_4 and Na_2TiO_3 filtered off. Ignite in a platinum crucible, fuse thoroughly with KHSO_4 , cool, dissolve in hot H_2O ; make 1 per cent acid with H_2SO_4 , heat to boiling, add 20 c. c. of 3 per cent H_2O_2 to oxidize Ti, and then precipitate the Zr phosphate as above. (4) Minerals containing Zr are analyzed by the same method as for Zr precipitates, except that if much Fe is present it must be reduced with $\text{Na}_2\text{S}_2\text{O}_3$ before precipitating Zr. (5) In Ni-Zr alloys dissolve and bake to dryness and filter off SiO_2 as usual. Make filtrate strongly ammoniacal and remove Ni by electrolysis. Filter off Fe, Al, and Zr precipitates, ignite, and treat ignited oxides as minerals are analyzed. Treat SiO_2 , if necessary, for Zr present. (6) In treating all SiO_2 precipitates with HF , when Zr is present, an equal amount of H_2SO_4 at least must be used (an excess is desirable) to prevent loss of Zr as ZrF_4 . (7) Scant Zr precipitates should stand 24 hours before filtering.

DETERMINATION OF ZIRCONIUM (IN STEEL).

The method of the United States Bureau of Standards is as follows:^b

Dissolve 1 gram in a mixture of 30 c. c. sulphuric acid (dilute 1:1), 15 c. c. hydrochloric acid, and 10 c. c. nitric acid.

^b Private communication.

Heat until dissolved and evaporate to fumes of sulphuric anhydride. Cool, take up with 60 c. c. water and 15 c. c. hydrochloric acid. Filter; wash the residue with hot water and dilute hydrochloric acid. In the filtrate precipitate iron and zirconium by ammonia in slight excess; filter without boiling and wash the precipitate twice on the filter with hot water; reject the filtrate.

Dissolve the precipitate in a little hydrochloric acid, washing the filter with hot water and collecting the solution and washings in the original beaker.

Nearly neutralize the solution with ammonia, finishing up with ammonium carbonate, which is added until a slight permanent precipitate forms; redissolve with a few drops of dilute hydrochloric acid and add 1 c. c. in excess. Dilute to 300 c. c. and saturate with sulphur dioxide gas. Then boil until the solution only smells faintly of sulphur dioxide and zirconium is precipitated with any titanium that may be present.

Filter and wash with hot water and dilute sulphurous acid.

Repeat neutralization and precipitation with sulphurous acid if necessary.

Dry, ignite, and weigh as zirconium dioxide. If titanium is present, fuse the ignited oxides with 2 grams of potassium bisulphate, dissolve with dilute sulphuric acid, and determine titanium present by reduction with zinc as described in volumetric method for determination of titanium and deduct titanium dioxide found from weight of ignited oxides.

USE OF CUPFERRON IN ANALYSIS FOR ZIRCONIUM.

Brown³⁴³ gives this procedure:

The cupferron reagent can be used in acid solution for the quantitative precipitation of Fe, Ti, and Zr from solutions containing these elements mixed with Al and Mn. The Fe was separated by dissolving the oxides (obtained from igniting the precipitate) in KHSO_4 and H_2SO_4 , precipitating with H_2S , tartaric acid and NH_4OH in the usual way, dissolving the FeS in HNO_3 , precipitating as hydroxide, and igniting. Ti and Zr in the filtrate were obtained by evaporation almost to dryness, heating in a Kjeldahl flask with H_2SO_4 and HNO_3 to destroy all tartrate, and then proceeding in either of three ways: (a) Ti and Zr were precipitated as hydroxides with NH_4OH dissolved with KHSO_4 , treated with H_2SO_4 , and Ti reduced and titrated with KMnO_4 . Zr was obtained by difference. (b) The oxides were weighed together and dissolved as in method (a) and Zr precipitated with Na_2HPO_4 and H_2O_2 in dilute H_2SO_4 ; the precipitation was repeated to remove Ti which was carried down, and the phosphate was fused with Na_2CO_3 , extracted, filtered, washed, fused with KHSO_4 , dissolved with H_2SO_4 , precipitated with NH_4OH and weighed as ZrO_2 . (c) Ti was determined colorimetrically by the use of H_2O_2 and the same portion was used to determine Zr by method (b). Al and Mn were separated with the usual HNO_3 and KClO_3 method when much Mn was present, and the Mn was precipitated and weighed as pyrophosphate. When little Mn was present, the filtrate from the cupferron precipitation was evaporated with H_2SO_4 and HNO_3 to destroy the excess reagent, and two precipitations of the Al with NH_4OH were used. Details are given of the application of these methods to the analysis of baddeleyite and zircon.

The method for the preparation of cupferron is given by Baudisch and King^{342a}, as described on page 73.

ZIRCONIUM IN ALLOYS.

The methods of analysis used in the laboratories of the Titanium Alloy Manufacturing Co. are essentially the same as for titanium, which are described below:

Volumetric method for determination of titanium.—The volumetric method used for determination of titanium is essentially that described by P. W. and E. B. Shimer in the Proceedings of the Eighth International Congress of Applied Chemistry, the method hereinafter described differing principally in the form of reductor and also in a few details of operation.

Reagents.—Standard ferric ammonium sulphate solution. Dissolve 30 grams of ferric ammonium sulphate in 300 c. c. water acidified with 10 c. c. of sulphuric acid; add potassium permanganate drop by drop as long as the pink color disappears, to oxidize any ferrous to ferric iron; finally dilute the solution to 1 liter.

Standardize this solution in terms of iron. The iron value multiplied by 1.4329 gives the value in titanous oxide (TiO_2); and the iron value multiplied by 0.85046 gives the value of the solution in terms of metallic titanium.

Indicator.—Saturated solution of potassium thiocyanate.

Reductor.—As a reductor a 500-c. c. dispensing burette is used. The internal dimensions of the burette are $1\frac{1}{2}$ inches by 22 inches. The reductor is charged with 1,200 grams of 20-mesh amalgamated zinc, making a column about 12 inches high with an interstice volume of about 135 c. c. This form of reductor is convenient, and when used as hereafter described is adapted to maintaining hot solutions, which is essential for complete reduction of the titanium. The reductor is connected to a liter flask for receiving the reduced titanium solution through a three-hole rubber stopper, which carried also an inlet tube for carbon dioxide supply, and an outlet tube for connecting with the suction pump.

Method.—Determination of titanium in ferrocen-titanium: One-half gram of the sample is dissolved in a 6-inch porcelain evaporating dish in a mixture of 10 c. c. of water, 10 c. c. sulphuric acid, 5 c. c. hydrochloric acid, 5 c. c. nitric acid.

The solution is evaporated to fumes of sulphuric anhydride; taken up by boiling with hot water and hydrochloric acid. The filtrate and washings should be about 100 c. c. in volume.

The reductor is prepared for use by first passing through it a little hot dilute sulphuric acid followed by hot water, finally leaving enough hot water in the reductor to fill to the upper level of the zinc.

The hot titanous solution prepared as described above is now introduced; about 100 c. c. of water being drawn from the reductor into the original beaker to bring the solution to about the upper level of the zinc. The water thus removed will not contain any titanium if the operation has been conducted as described but serves as a safeguard; it is also convenient to acidify this water with 10 c. c. sulphuric acid and reserve it on the hot plate to be used as an acid wash after the reduction of the sample solution.

The titanium solution is allowed to remain in the reductor for 10 minutes.

While the solution is being reduced, the receiving flask is connected to the reductor and the air completely displaced by carbon dioxide, conveniently drawn from a cylinder of the liquefied gas.

When the reduction is complete, the receiving flask is connected with the suction pump, and while still continuing the flow of carbon dioxide the reduced solution is drawn out, followed by the reserved acid wash and then three or four 100 c. c. washes with hot water. The displacement of the sample solution

and the washing of the zinc are so regulated by means of the stopcock that the reductor is always filled with solution or water to the upper level of the zinc.

When the washing is complete, gradually release the suction to prevent acid being drawn back into the receiving flask.

Disconnect the flask, add 5 c. c. of potassium thiocyanate solution as indicator and titrate immediately with standard ferric ammonium sulphate solution, adding the solution rapidly until a brownish color is produced, which will remain for at least 1 minute.

The method is also well adapted for determining titanium in other titanium products, suitable means being employed for bringing the titanium into sulphuric acid solution.

DETERMINATION OF ZIRCONIUM IN STEEL.

(Adaption of method described in Journal of American Chemical Society, vol. 25, p. 426.)

Three-gram sample dissolved in sulphuric and hydrofluoric acids evaporated to SO_2 fumes, silica volatilized with hydrofluoric acid, residue added to filtrate, iron reduced with ammonium bisulphite or sodium thiosulphate solution quickly neutralized with ammonium hydroxide and then made slightly acid with about 6 drops of 1 : 1 hydrochloric acid, now add 1 to 3 c. c. phenylhydrazine, precipitate filtered off and washed with phenylhydrazine sulphite.

Precipitate dissolved and reprecipitated, ignited, and weighed as zirconium oxide plus aluminum oxide, precipitate then fused with sodium carbonate, melt dissolved in water. Sodium zirconate filtered off, aluminum precipitated and determined from filtrate and subtracted from the combined weights of the zirconium and aluminum oxides. The sodium zirconate may also be dissolved and the zirconium determined on this either as oxide or as phosphate.

NOTES ON THE ANALYSIS OF ALLOYS OF NICKEL AND ZIRCONIUM.

Kelley and Myers³⁶⁹ describe a convenient works-laboratory method for the analysis of an alloy of the following approximate composition:

	Per cent.		Per cent.
Carbon-----	0.1 to 0.5	Aluminum-----	0.5 to 10.0
Nickel-----	70.0 to 90.0	Zirconium-----	2.0 to 18.0
Iron-----	2.0 to 6.0	Tungsten-----	0.5 to 10.0
Silicon-----	2.0 to 8.0	Manganese-----	0.1 to 0.3

An outline of the method used is as follows:

Dissolve 1 gram of the material, preferably of a fineness to pass a 40-mesh sieve, in 40 c. c. of hydrochloric acid, to which 20 c. c. of nitric acid have been added; then evaporate the solution with 20 c. c. of sulphuric acid (specific gravity 1.58) until SO_2 fumes appear. On diluting with water the salts dissolve. Filtering separates nearly all of the tungsten as WO_3 and the silicon as SiO_2 , the zirconium appearing almost entirely in the filtrate.

Ignite the precipitate in a weighed platinum crucible. The first weight gives the weight of SiO_2 , WO_3 , and impurities. Then treat the residue with hydrofluoric and sulphuric acids to remove SiO_2 , which is determined by the loss in weight; fuse the residue which now remains with sodium carbonate, leach with water, and filter. The residue from leaching is generally very small and

should be ignited in the original crucible and its weight subtracted from the weight of the crucible contents after the removal of SiO_2 ; this gives the weight of WO_3 . If extreme care is to be used in the determination of the tungsten, this residue should be fused with KHSO_4 , leached in dilute HCl , and precipitated with ammonia. Under these circumstances iron, aluminum, and zirconium are precipitated free from sodium compounds which may contaminate the first residue. Upon ignition a correct residue is obtained to be subtracted from the weight of impure WO_3 . When such care is not necessary, the residue may be fused with the filtrate from the WO_3 precipitate.

By following the procedure as outlined above, the filtrate from the WO_3 contains in solution all of the iron, nickel, aluminum, and zirconium. The solution should be made up to a convenient volume, such as 200 c. c., and one-half taken for the iron determination.

To determine the iron, make the solution alkaline with ammonia and boil or heat near the boiling point for a short time; filter and wash the precipitate. Transfer the bulk of the precipitate to a beaker and wash the paper by running through it a small amount of dilute sulphuric acid. Add enough sulphuric acid to the beaker to dissolve the precipitate and an excess equivalent to 10 c. c. (specific gravity 1.58). Then pass the solution through a Jones reductor and determine the iron by titration with KMnO_4 .

To the other half of the solution add ammonia in excess, and remove the nickel by electrolysis. The presence of this small amount of iron and aluminum does not seem to interfere, but in doubtful cases the nickel may be dissolved in hydrochloric acid, evaporated with sulphuric acid diluted, and the iron and aluminum precipitated with ammonia; any iron and aluminum found in this way should be dissolved in a small amount of acid and added to the original electrolyte which now contains all of the iron, aluminum, and zirconium. The ammoniacal solution of nickel is now free from the elements just named and is available for analysis by electrolysis or by the precipitation of its nickel content with dimethylglyoxime. In the event of using the latter procedure, one-tenth of the solution is sufficient for the purpose.

Boil the solution containing Al, Fe, and Zr until nearly all of the ammonia has been driven off; then allow it to settle and filter, washing the precipitate with water. The precipitate contains, Al, Fe, and Zr. After transferring the precipitate to a beaker, dissolve in a minimum quantity of hydrochloric acid; then add solid KOH in excess to precipitate iron and zirconium, and leave aluminum in solution. Boil the mixture for 1 minute, allow to settle, and filter, washing the precipitate with water. The filtrate contains the aluminum; make this solution acid with HCl and then barely ammoniacal; boil a few minutes, filter, and wash. Then dissolve the precipitate in HCl and add 7 to 10 c. c. of sulphuric acid (specific gravity 1.58); evaporate the solution until fumes appear; cool, dilute, and filter to remove SiO_2 . Again add ammonia in slight excess and after brief boiling remove the $\text{Al}(\text{OH})_3$ by filtration; ignite and weigh as Al_2O_3 .

Dissolve the precipitate of iron and zirconium hydroxides which was separated from the aluminum in HCl (1:1) and reprecipitate with ammonia while boiling. The ignited precipitate contains Fe_2O_3 and ZrO_2 . Convert the iron found by titration into Fe_2O_3 and subtract its weight from the weight of Fe_2O_3 and ZrO_2 . This gives the weight of ZrO_2 .

If manganese is to be determined, weigh 1.5 grams of the material instead of 1 gram. Then determine manganese in one-third of the filtrate from the tungstic oxide. For this purpose add ammonia and ammonium persulphate to the solution before boiling. Wash and dissolve the precipitate in nitrate acid with

the addition of a little sodium sulphite or hydrogen peroxide to aid solution. The manganese is then ready for oxidation by sodium bismuthate and determination by the various known methods.

ZIRCONIUM DETERMINATION IN SAND.

Schiotz³⁸⁵ gives the following method:

Fuse the sample with NaOH and Na₂O₂ and remove the SiO₂ and H₂S precipitated metals in the usual manner. Render the solution fairly acid with H₂SO₄ and add H₂O₂ until there is no further change in color, after which make up the solution to a definite volume and remove an aliquot representing about 0.1 gram ZrO₂. To this portion add 10 c. c. of concentrated H₂SO₄, also some H₂O₂, and then dilute until the H₂SO₄ is about 10 per cent. Precipitate the Zr by adding 10 per cent solution Na₂HPO₄. Wash the precipitate with dilute H₂SO₄ by decantation as long as any color can be removed and then work up with the least necessary amount of water in the beaker and dissolve in 25 to 30 c. c. boiling concentrated H₂SO₄. Pour this solution into 300 c. c. water, add H₂O₂, and reprecipitate with Na₂HPO₄. As it is impossible completely to wash this precipitate, wash several times by decantation and then dry and fuse with NaOH. Digest the fused mass with water and acidulate with HCl, filter, wash dry, ignite, and weigh as ZrO₂. Th and Ti are completely separated by this procedure.

ESTIMATION AND SEPARATION OF TITANIUM, COLUMBIUM, TANTALUM, AND ZIRCONIUM.

Headden³⁶⁴ gives this procedure:

TiO₂ from Ta₂O₅.—Fuse with KHSO₄, pulverize, treat with H₂O, bring into complete solution by adding a little dilute HF, add NH₄OH till slight permanent precipitate is produced, dissolve this by adding 7 to 10 grams NH₄F; then add 5 to 8 grams (NH₄)₂CO₃, 5 to 10 c. c. H₂O₂, and heat to boiling. The volume should be 150 to 200 c. c. Pour while boiling into a boiling 3 per cent solution of (NH₄)₂CO₃ and continue to boil 30 minutes after the solution becomes turbid. The precipitated material consists of Ta₂O₅ contaminated with TiO₂ and must be dissolved in dilute HF and reprecipitated until the filtrate gives no precipitate with NH₄OH. The precipitate is then ignited and weighed. The average of four determinations gave 99.3 per cent of the Ta₂O₅ taken.

Ta₂O₅ and Nb₂O₅.—Fuse bisulphate, dissolve with the aid of HF, neutralize, add 4 grams NH₄HCO₃ to strong alkaline reaction, heat on water bath 60 to 70° for 45 minutes. The Ta₂O₅ which precipitates is somewhat contaminated with Nb₂O₅, and the test results range from 97.5 to 106.7 per cent of the Ta₂O₅ taken.

TiO₂ from ZrO₂.—The acid solution containing the oxides is neutralized or made slightly alkaline with NH₄OH, NH₄F added until the precipitate dissolves, heated to boiling, and NH₄OH added. Continue the boiling one minute and filter out the TiO₂. The ZrO₂ may be determined by expelling F with H₂SO₄, dissolving in H₂O, and precipitating with NH₄OH. Test results show the method to be entirely accurate.

ZrO₂ from NbO₅.—To the acid solution add 3 grams NH₄F, heat until clear, cool partly, add excess of NH₄HCO₃, boil 8 to 10 minutes, remove from heat, add large excess NH₄OH, allow to cool, and filter. Reprecipitation is necessary. The results show ZrO₂ about 5 per cent too high and Nb₂O₅ correspondingly low.

CHAPTER VI.—ZIRCONIUM METAL.

PREPARATION.

The literature contains references to at least three forms of zirconium: Amorphous, crystalline, and graphitic. The authors substitute for the solid metal the name sintered or coherent. The methods of preparation of these varieties of the metal are given below.

AMORPHOUS ZIRCONIUM.

Amorphous zirconium has been prepared in a number of different ways:

Berzelius³⁹⁸ reduced potassium fluozirconate (K_2ZrF_6) with potassium by heating the two intimately mixed together in an iron dish at a red heat. The mass was cooled, treated with dilute hydrochloric acid and ammonium chloride solution to extract the soluble salts. The finely divided gray-black metal was then washed with alcohol and dried. This procedure gives a product of questionable metal content which always contains a considerable amount of oxide.

Troost⁴²² has obtained amorphous zirconium by passing $ZrCl_4$ vapors over heated sodium. The finely-divided amorphous metal deposits on the sides of the tube in which the heating is done.

Phipson⁴¹⁶ and also Winkler⁴⁴² claim to prepare zirconium by heating zirconia with magnesium or zinc. They obtain by heating these two materials together a velvet black powder having the appearance of wood charcoal. This material, when the experiment is performed in hydrogen, consist largely of hydride; without the hydrogen only a partial reduction is realized.

Weiss and Neumann⁴⁴⁰ have reduced the double fluorides with sodium, in slight excess of equivalent quantities, in an iron cylinder. The mixture is placed in the tube covered with a layer of KCl or NaCl; the tube is closed and heated to perhaps $1,000^\circ$ C. After cooling the mass is washed with cold water and absolute alcohol and dried. Under the best of conditions this procedure yields 97 to 98 per cent zirconium.

Wedekind⁴³⁵ who has made exhaustive studies of the preparation and properties of zirconium suggests that the oxide (ZrO_2) be reduced with metallic calcium. This author in cooperation with Kuzel⁴⁰⁶ has carried out the reduction as follows: 50 grams pure ZrO_2 and 64 grams calcium are placed in an iron tube which is closed at the bottom and has a cap so that it can be evacuated and sealed air tight. The tube is 36.5 cm. long and 6.5 cm. in diameter. After the tube is charged, it is heated to 80 to 90° C. and evacuated to 0.5

to 1 mm. pressure. The tube is then heated in a strong flame. The reaction can be observed when the tube glows at the point of reaction. The tube is cooled after the reaction is complete and the contents washed with water, dilute hydrochloric acid, and alcohol, away from the air as much as possible. The powder is then dried at 250° to 300° C. in a desiccator under a high vacuum. This method gives about 97 to 98 per cent zirconium, according to the authors.

CRYSTALLINE ZIRCONIUM.

Troost⁴²² first prepared the so-called crystalline zirconium by heating potassium fluozirconate with $1\frac{1}{2}$ parts of aluminum in a carbon crucible at the melting temperature of iron. When the melt cools, crystals appear on the surface of the metal alloy, which settles to the bottom of the dish. After treating with hydrochloric acid to remove the excess of aluminum, Troost claims to obtain crystals containing only a small quantity of aluminum.

Moissan⁴¹⁴ obtained what he called crystalline zirconium containing some carbon by reducing the oxide in a carbon crucible with a carbon arc, using a current of 360 amperes and 70 volts. Moissan claims also that metallic zirconium may be prepared by the suitable interaction of zirconium carbide and oxide. This metal obtained in this way is very different from the metal obtained by the aluminum reduction of K_2ZrF_6 and should perhaps be listed under sintered or coherent metal.

Troost⁴²³ has prepared ZrC in the electric-arc furnace and later heated the carbide thus prepared with the oxide to get the metal containing more or less carbon. In this way he obtained metal very similar to that of Moissan.

The same author⁴²² states that he obtains crystalline zirconium by the electrolysis of the fused potassium fluozirconate. Crystals of this substance form very brilliant platelets and are separated from the cooled mass by extracting the soluble salts with water.

Weiss and Neumann⁴⁴⁰ have made the reduction in the following manner: 1 part of K_2ZrF_6 is heated in a carbon dish till well melted. One and one-half parts of aluminum are added a little at a time. The reaction is completed in 10 to 15 minutes, after which the mass is covered with a layer of KCl and allowed to cool. The metal collects in the bottom of the crucible. After treating the metal, first with caustic soda and later with hydrochloric acid, a crystalline alloy is obtained that contains 72.2 per cent Zr and 27.5 Al .

GRAPHITIC ZIRCONIUM.

According to Ohly^{415a}, heating sodium zirconate with iron yields graphitoidal zirconium in the form of very small light scales of a

steel-gray color. This method was first used by Troost⁴²². It is doubtful whether any very pure metal could be prepared in this way.

SINTERED OR COHERENT ZIRCONIUM.

Kuhne⁴⁰⁵ has patented a method for the reduction of refractory oxides such as TiO_2 , V_2O_5 , ThO_2 , CeO_2 , and ZrO_2 with the aluminothermic method. He gives as his example the reduction of titanite oxide.

TiO_2 , 80 parts; Al, 54 parts; BaO_2 , 169 parts, according to the equation: $\text{TiO}_2 + \text{Al} + \text{BaO}_2 = \text{Al}_2\text{O}_3 + \text{BaO} + \text{Ti}$.

Weiss and Neumann⁽⁴⁴⁰⁾ have suggested the production of fused zirconium by the aluminothermic reduction of ZrO_2 , using a mixture of Al and KClO_3 to produce enough heat for the reaction.

Weiss and Neumann have also prepared the coherent (or sintered) metal from the so-called crystalline zirconium prepared by the reduction of the potassium fluozirconate with aluminum. This material, which contains 72.2 per cent Zr and 27.5 per cent Al, is pressed into rods 1 to 2 cm. in diameter, and these are arced with a current of 60 to 80 amperes at 20 volts in an evacuated atmosphere of nitrogen or ammonia. It is claimed that the aluminum is volatilized by the heat and the zirconium is sintered to give a very pure metal of 99 per cent or better.

Kuzel and Wedekind⁴⁰⁶ state that if their amorphous zirconium is heated above $1,000^\circ \text{C}$. in a high vacuum, the metal powder sinters or welds itself into granules and small compact lumps. It is claimed that as high as 99.09 per cent Zr has been obtained by this method.

Although Moissan and Troost^{414, 423} call their metal crystalline, its properties are those described under sintered or coherent metal.

PROPERTIES OF ZIRCONIUM METAL.

The literature shows great disagreement regarding the properties of zirconium, partly because the different varieties of the metal have been confused, and partly because of the difficulty of preparing pure products. The coherent metal after proper heat treatment shows decided crystalline structure under the microscope, but many of the references in the literature to crystalline zirconium describe the aluminum alloy.

AMORPHOUS ZIRCONIUM.

The production of very pure amorphous zirconium has proved difficult because of the great ease with which the metal in this form combines chemically with oxygen, nitrogen, carbon, silicon, and other elements, and because of the great tenacity with which the amorphous metal clings to moisture and absorbs gases. It is doubtful whether any of the early authors on amorphous zirconium described anything like pure zirconium. Kuzel and Wedekind claim

that if amorphous zirconium is to be completely deprived of gases it must be heated under a high vacuum to about $1,000^{\circ}\text{C}$.

These few statements aid in explaining the discrepancies in the literature. Moreover, in some of the papers on the subject the properties of the different varieties of metal are confused, and it is difficult to select data that will ultimately prove most nearly correct. It is perhaps true that the amorphous metal that has been sintered together should be grouped separately from the metal that has been fused to a solid white metal in the process of formation. The sintered amorphous metal as it has been prepared heretofore is sure to contain oxide or nitride, and the fact that, according to Wedekind and Kuzel, the amorphous sinters at $1,000^{\circ}\text{C}$. is, perhaps, indicative that impurities are present; or it must be that the metal softens far below its melting point. The specific gravity of amorphous zirconium, for example, is given as 4 to 6, and the melting point also varies within wide limits.

TABLE 4.—*Properties of amorphous zirconium.*

Physical Properties.

Atomic weight	90.6
Alloys	Does not form alloy readily.
Boiling point	?
Brittleness	
Corrosion	Remains unchanged at ordinary temperature.
Color	Gray to black metallic.
Electrical conductivity	Very low.
Electromotive force (solution pressure)	Not given.
Expansion and contraction	?
Fusibility	Sinters at $1,000^{\circ}$ (Wedekind and Kuzel).
Hardness	Soft.
Luster	Metallic when polished.
Magnetic permeability	Paramagnetic.
Melting point	$1,530^{\circ}$ (?).
Occlusion of gases	Very great.
Odor	Metallic, like ozone.
Plasticity	None.
Specific heat	0.066.
Specific gravity	4.1 at 18°C . (about).
Structure	Uniform (without crystalline form) under microscope.
Tensile strength	None.
Thermal conductivity	Very low.
Volatility	Does not volatilize at $3,000^{\circ}\text{C}$.
Welding power	
Spectrum	Numerous bands in violet and ultra violet.

Chemical Properties.

Action toward chemical reagents:

Chlorine	Combines readily at comparatively low heat (50° C.).
Nitrogen	Burns to nitride at dull red heat.
Oxygen	Burns to oxide at dull red heat, with dull red glow.
Hydrochloric acid	Slowly soluble in 1:1 hot acid.
Hydrofluoric acid	Readily soluble.
Nitric acid	Nearly insoluble.
Sulphuric acid	Slowly soluble in hot concentrated.
Fused sodium bisulphate	Dissolves readily.
Fused caustic soda or fused sodium carbonate	Dissolves slowly on continued fusion.

CRYSTALLINE ZIRCONIUM.

As it is doubtful whether crystalline zirconium (Zr_3Al_4) has been prepared free of other metals, the values given for this variety of metal may or may not be correct. Only a few values are listed here, as more representative of the properties of a high percentage zirconium-aluminum alloy than of pure zirconium. These properties are said to be mostly those of the material obtained by the aluminum reduction of the double fluorides.

TABLE 5.—*Properties of crystalline zirconium.*

Physical Properties.

Alloys	Forms alloys readily.
Color	White, sometimes yellowish, due to superficial nitride formation.
Crystalline form	Monoclinic.
Electrical conductivity	High.
Hardness	7 to 8 Mohs' scale (scratches quartz).
Melting point	1,300 to 2,350° C.
Luster	Bright.
Plasticity	Brittle.
Specific heat	0.066 to 0.08.
Specific gravity	4.15 to 6.
Thermal conductivity	High.

Chemical Properties.

Action toward chemical agents:

Chlorine	Burns in chlorine, at a dull red.
Nitrogen and oxygen	Resists action at red heat.
Aqua regia	Soluble in boiling aqua regia.
Hydrochloric acid	Insoluble.
Hydrofluoric acid	Soluble.
Nitric acid	Insoluble.
Sulphuric acid	Insoluble.
Fused alkalis, bisulphates, etc.	Slowly soluble.

GRAPHITIC ZIRCONIUM.

As there are very few references in the literature to the so-called graphitic zirconium, its properties can not be given. There is scarcely enough proof of the existence of such a variety to warrant mention.

SINTERED OR COHERENT ZIRCONIUM.

As regards the properties of sintered or coherent zirconium, no one in the literature claims better than 99 per cent Zr. One per cent of silicon or iron may decidedly alter the properties of the sintered metal.

TABLE 6.—*Properties of coherent zirconium.*

Physical Properties.

Atomic weight	90.6.
Alloys	Does not alloy readily with iron by direct addition.
Boiling point	Not given; very high.
Brittleness	Very brittle.
Corrosion	Does not corrode.
Color	White yellowish color due to superficial nitride formation.
Electrical conductivity	High.
Electromotive force	Not given; probably between iron and copper.
Fusibility	Very infusible.
Hardness	Said to be very hard; will scratch glass.
Luster	Takes brilliant white polish.
Magnetic permeability	Paramagnetic.
Melting point	(?) 1,530° (perhaps higher).
Odor	None.
Specific gravity	6.2.
Specific heat	0.0804.
Thermal conductivity	High.
Volatility	Very small.

Chemical Properties.

Action toward chemical agents:

Chlorine	Combines with chlorine at red heat.
Nitrogen and oxygen	Burns in oxygen or nitrogen at white heat.
Aqua regia	Dissolves on long boiling.
Hydrochloric acid	Insoluble.
Hydrofluoric acid	Slowly soluble on heating.
Nitric acid	Insoluble.
Sulphuric acid	Insoluble.
Fused alkalis, bisulphates, etc.	Goes into solution on long-continued heating.

As has been indicated before, the writers are by no means sure that the data given above, especially for the sintered metal, are near the values that will be later found for the pure 100 per cent metal. It is doubtful if any of the data listed above have been accumulated from metal having more than 98 per cent zirconium.

CHAPTER VII.—ZIRCONIUM ALLOYS.

Very few accurate data are available on zirconium alloys. Until recently the statement that zirconium did not alloy with iron was accepted. Grenagle, Brown, Weiss, and others, however, have lately employed and patented methods covering alloys of zirconium with iron. The indications are that zirconium imparts to alloyed metals an increased tensile strength, toughness, and a certain degree of malleability. The data, however, are conflicting and the properties may be imparted either by the zirconium itself or by a combination of metals and metalloids of which the zirconium forms a part.

Stimulus was recently given this question by the discovery that small percentages of zirconium in steel increased the tensile strength and hardness remarkably; and an investigation of zirconium steel and its application to war purposes has been made by the Bureau of Mines.^c

In collecting this bibliography and in studying the metallurgy of zirconium metal, references to zirconium alloys, the properties, effects of varying percentage of different constituents, and methods of production of those alloys were carefully compared, and a historical review of the literature is presented below.

Grenagle^{402a} has patented a method for producing ferrozirconium by means of the alumino-thermic reduction process. He claims that ferrozirconium of 60 to 90 per cent zirconium is malleable, ductile, and has good tensile strength. Enhanced strength and toughness are given to ferrozirconium by 0.1 to 0.3 per cent titanium. The binary ferrozirconium alloys can not be used for cutting tools. Grenagle claims that although zirconium and iron do not alloy readily by direct addition if they are reduced together simultaneously, the constituent metals form homogeneous alloys of varying composition depending on the relative quantities of the materials employed and the conditions of reduction. These alloys (he claims) exhibit no tendency to oxidize and are highly resistant to chemical agents. Alloys may be produced that are more or less malleable and ductile, take high polishes, and have a silver-white steel-like luster. They have, it is claimed, important uses for lamp filaments, transformer elements, etc. Grenagle gives the equation representing his reduction as follows:



^c Gillet, H. W., and Mack, E. L., Alloy steels: Bull. 199, Bureau of Mines. In preparation.

Later authors say, however, that ferro alloys having more than 30 per cent zirconium are too brittle to have commercial uses.

Brown^{399a} has also patented the same process. According to Cooper^{399c}, an alloy of zirconium, with nickel or cobalt, with or without the addition of other metals, forms tough alloys that are resistant to acids and alkalis and when heated to 1,150° C. form thin adherent coatings of oxide which prevent further oxidation of the metal. When 2 to 10 per cent Zr is used and the rest is nickel, the alloy is suitable for knives, razors, etc. Cutlery made from the Zr alloy of nickel remains bright and clean even under the action of the acids of such fruits as lemons. The alloy can be worked at a red heat and is applicable for electrical uses in toasters, irons, and other domestic utensils. Alloys of 25 to 30 per cent Zr and Ni are used for high-speed cutting tools. Other metals are sometimes added to raise the melting point or hardness of the metal. The alloys are made by the alumino-thermic reduction according to the following equation:



Cooper has also patented other zirconium alloys for somewhat the same purposes, having the following composition:

Composition of zirconium-nickel alloys.

Element.	Per cent.		
Al-----	7.92	7.70	7.48
Si-----	3.80	3.50	3.40
Zr-----	6.48	6.30	6.12
Ni-----	78.00	75.50	71.00
W-----	4.00	7.00	12.00

In still another patent Cooper prepares an alloy of the following composition: Al, 8.36; Si, 3.80; Zr, 6.84; Ni, 81.

The method of producing this latter alloy is as follows: Grind 66 pounds nickel oxide and 36 pounds Brazilian zirkite to pass a 200-mesh sieve and thoroughly mix with 32 pounds of 200-mesh aluminum. Place mixture in a nickel crucible of conical shape lined with magnesia or alumina. Ignite the charge with magnesium ribbon. The alloys may be tapped off into molds, remelted, and further purified to give the desired percentage composition.

Ludwig Weiss⁴⁴¹ has patented a method for producing sound metal castings. He introduces zirconium, added in the form of carbide, silicide, etc., directly to iron, gun metal, brass, copper, aluminum, bronze, or the like and dissolved in them. According to him 1 per cent of zirconium is enough to give the maximum strength to these metals. Metals alloyed with zirconium are claimed to have greater strength than those alloyed with aluminum, also they are said to have

greater hardness and elasticity, and are suitable for castings, construction, or engineering work.

Kelly and Miller ^{406a} have assigned to the Midvale Steel Co. a patent covering a high-speed cutting tool of the following composition: C, 0.1 per cent; Ni, 86.4 per cent; Al, 6 per cent; Si, 6 per cent; Zr, 1.5 per cent.

These authors state that the zirconium may range from 0.5 to 2 per cent. A larger proportion of zirconium is not prohibitive, but where silicon and aluminum are present in the required proportions an excess of zirconium is without benefit and may be harmful.

Anderson ^{394a} says:

Ferrozirconium is made by the reduction of zirconia with aluminum by the thermit process and is produced so as to contain upward of 3 per cent zirconium. In England a 20 per cent ferrozirconium has been used to a subordinate extent in place of ferrotitanium in scavenging steel. The zirconium-bearing steels are reported to be adapted for bullet-proof sheets, armor plate, and armor-piercing projectiles. Both ferrozirconium and ferrochromium zirconium were made in small lots in the United States in 1918.

According to Meyer ⁸⁸:

It had been known prior to our entry into the war that the Germans had developed remarkable zirconium steel, which was claimed to be superior to vanadium, chromium, molybdenum, tungsten, or nickel steel. The demand for light armor plate on tanks, aeroplanes, and other equipment compelled the Government to investigate the possibilities of all steel-hardening elements for such purposes, and it was ultimately decided that zirconium was the best suited for the requirements of the War Department. Owing to the lack of authoritative technical data on the production and uses of ferrozirconium, many difficulties were encountered, but ultimately, through the efforts of several large manufacturers of ferroalloys, a ferrozirconium suitable for the production of zirconium steel was evolved. Ferrozirconium as now offered to the trade carries 30 to 36 per cent zirconium metal and sells for \$4 to \$4.50 per pound of contained metal, depending on the quantity demanded. It is not to be supposed that ferrozirconium will supplant ferrotungsten, ferrochromium, or ferrovanadium, but it seems evident that it will be largely in demand for certain purposes for which other ferroalloys are not entirely satisfactory.

It is claimed that ferrozirconium can be prepared in the arc furnace directly from zirkite ore. The alloy, of course, would contain much silicon, but should not cost anything like \$4 a pound. The zirkite ore is listed at 6 to 7 cents a pound.

PART II.—EXPERIMENTAL WORK ON ZIRCONIUM.

CHAPTER VIII.—EXAMINATION OF ORES AND ORE-DRESSING EXPERIMENTS.

The information to be gained from the literature on the mining and concentration of zircons (particularly American zircons) is meager. As the American zircons contain many impurities, chiefly compounds of titanium, silicon, and iron, it is necessary in utilizing them for the production of pure salts of zirconium to remove as much as possible of the impurities by the methods of ore concentration.

The ores supplied for the tests were high-grade zircon, zircon sands from Pablo Beach, Fla, and Brazilian zirkite ore. In the examination of zircon sands and in ore-dressing experiments with them results were obtained which, although not thoroughly investigated, promise to yield methods of obtaining high-grade zircons from low-grade sands. It may be possible that by the treatment suggested below, American zircon can successfully compete with the Brazilian ores.

The high-grade zircon, which was examined first, gave the analysis following:

Analysis of high-grade zircon.

ZrO ₂	71.70
Fe ₂ O ₃	7.07
Al ₂ O ₃	2.91
TiO ₂	6.00
SiO ₂	13.00
Total	100.00

The Brazilian mineral zirkite was used for the preparation of the oxide of zirconium and for the many experiments made on the methods of fusion of the ores. All of the zirkite used for ore fusions was first ground to pass a 100-mesh sieve.

A typical analysis of the Brazilian zirkite is appended:

Analysis of Brazilian zirkite.

SiO ₂	19.7
Al ₂ O ₃	1.2
Fe ₂ O ₃	2.98
TiO ₂	1.65
ZrO ₂	74.45
	99.98

The third sample of ore examined was zircon sand from Pablo Beach deposits in Florida, which had been put through a Dings magnetic separator. Its analysis, stated in round numbers, was as follows:

Analysis of concentrate from Pablo Beach sands.

ZrSiO ₄	60.00
Fe ₂ O ₃	0.5 to 1.00
Al ₂ O ₃	Not determined.
TiO ₂	16.00
Free SiO ₂	20.00

Under the microscope the titanium seemed to be largely in the form of rutile rather than of ilmenite or other titaniferous ores. This material was too low grade and the titanium content was too high for convenient use in the production of zirconium salts. An attempt to purify it by running it through a Wetherill magnetic separator at the rate of 40 pounds an hour, with a current of 5 amperes and with the magnets one-fourth inch from the belt, met little success. The Wetherill magnetic separator was of the experimental type, having a 6-inch belt and two double-pole magnets. The magnets were wound for 30,000-ampere turns, using a maximum direct current of 5 amperes at 110 volts.

Concentration tests with a large card table, although there is not much difference in the densities of the materials, were very encouraging. The specific gravities of the minerals in the zircon sands are about as follows: ZrSiO₄, 4.7; TiO₂, 3.7 to 4.2; Al₂O₃, 3.7 to 4; SiO₂, 2.66.

The white silica could be seen on the lighter side of the table separated from the white zircon by a band of brown to purple colored material containing a high percentage of TiO₂. No attempt was made at a careful separation, but the analytical results are of interest.

From the tabling were obtained 45 per cent of concentrate, 30 per cent of middling, and 25 per cent of tailing. The analysis of these materials are given in Table 7:

TABLE 7.—*Analysis of table zircon sands.*

	Original.	45 per cent concentrate.	30 per cent middling.	25 per cent tailing.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
ZrSiO ₄	60	75	50	11
TiO ₂	16	5	40	17
SiO ₂ , by difference.....	24	20	10	72
Al ₂ O ₃				
<i>By microanalysis.</i>				
ZrSiO ₄	60	80	50	15
TiO ₂	18	5	40	14
Al ₂ O ₃ , by difference.....	22	14	10	71
SiO ₂ , by difference.....				

The micronanalyses were made by counting the particles of zircon and other materials in given fields of the microscope. The material was first classified to pass a 150-mesh sieve but not a 200-mesh. About 50 particles were counted in a field, and the average of several countings taken. In converting the results into percentage, the number of particles in the field were corrected for their respective specific gravities. It is interesting to note how closely the microscopic count checks the analytically determined values.

The analyses show that much of the titanium was removed by the tabling and that without doubt most of it could be removed in this way. Much of the free silica also could be separated. The removal of the titanium and the free silica would be of great value in purifying this material so that it could compete with the Brazilian zircons; although the Brazilian zircons undoubtedly have a larger percentage of available ZrO_2 , due to the baddeleyite with which they are always mixed. Crude Brazilian zirkite as it is sold in this country contains about 75 per cent ZrO_2 , whereas the zircons found in this country rarely contain as much as 60 per cent. However, the removal of the titanium and free silica will materially increase the value of this ore and render it suitable for treatment in preparing ZrO_2 . A screen analysis of the original sand is as follows:

Screen analysis of zircon sand.

	Per cent.
+ 65 mesh_	0.7
80 mesh_	2.4
100 mesh_	25.2
150 mesh_	58.5
200 mesh_	9.7
—200 mesh_	2.6

Because of the fineness of the sand grains it is suggested that a table similar to the Deister-Overstrom sliming table should give excellent results.

Some zircons are said to show radioactivity. Several samples of the sand were examined but the activity was found to be very small. In general the more impure the zircon the more activity is shown.

CHAPTER IX.—ORE FUSIONS.

The principal methods of ore treatment mentioned in the literature are:

- (a) Caustic soda fusions.
- (b) Soda ash fusions.
- (c) Niter-cake fusions.
- (d) Hydrofluoric acid treatment and fluoride fusions.
- (e) Heating with lime and coke; volatilization of zirconium tetrachloride.
- (f) Heating ore with fluorspar and sulphuric acid.
- (g) Sulphuric acid method of treatment of zirkite ore.

Each of these different methods has been tested with quantities of ore varying from 10 grams to 10 pounds. At first an attempt was made to use the proportion of ore to fusion mixture suggested in the literature. For some tests, however, this proportion did not give satisfaction and it was changed to obtain the best results. Also, in some tests modifications of the methods proved more suitable than the original methods. Some of the methods, when tried in the laboratory, gave such poor results that little work was done with them. Other methods requiring special apparatus received scant attention.

Caustic soda fusion proved the most satisfactory fusion method for ordinary work. It required a much lower temperature and a shorter period of fusion than any of the others, and the leached residues of the sodium zirconate were easy to handle. Second in favor is soda ash fusion, the chief objection to it being the relatively high temperature required. It also requires a larger fusion period than caustic soda. Niter-cake fusion decomposes a fair proportion of ore, but the great quantity of fumes given off make it objectionable. Moreover the solution of the niter-cake fusion is rather difficult to handle because of the formation, under certain conditions, of an insoluble double sodium zirconate sulphate.

FUSION WITH CAUSTIC SODA.

In fusion with caustic soda the best mode of procedure proved to be to fuse the caustic soda first. When that is completely fused, the ore finely pulverized in the proportion of 1 to every 6 parts of caustic soda is slowly sifted in, thus mitigating the violent frothing of the reaction. The fusion is conducted for $1\frac{1}{2}$ to 2 hours, a clear liquid fusion being maintained. The fused mass when cooled is crushed and then leached with water.

FUSION WITH SODA ASH.

Fusion with soda ash is conducted in a manner quite similar. The ore is mixed with at least 8 times its weight of the carbonate and the mixture fused. The fusion is more complete the longer it is conducted. In general, the melt is maintained in the molten condition for 3 hours, and is then cooled, crushed, and leached with water.

The caustic fusions are leached with hot water in the ratio of 1 gallon of water to every pound of roast. The method of treatment consists in heating the water and roast to the boiling point, allowing the mixture to stand, and decanting the clear liquid. The process is repeated twice. The third washing suffices to remove most of the free alkali. Much more washing causes the formation of finely divided zirconium hydroxide which is difficult to filter and wash. Only a part of the silica is removed by this treatment as double sodium zirconium silicate is formed which is insoluble in water but is readily decomposed by acids.

Dilute acid digestions of the residues after leaching with water are not to be recommended, as much of the silica goes into solution and causes a great deal of difficulty in subsequent purification. If the acid is diluted too much, insoluble basic salts of zirconium are formed. Concentrated acids are to be preferred as they will, when evaporation is carried down nearly to dryness, eliminate most of the silica. When concentrated sulphuric acid is used the solution is carried to fumes and heated for a short time at this temperature. It is then cooled, the zirconium sulphate dissolved in cold water and filtered from the silica and the insolubles.

FUSION WITH NITER CAKE.

The niter-cake fusions are conveniently performed in a cast-iron vessel. The niter cake is first fused and the finely pulverized ore is slowly added. Good results are not obtained with less than 15 parts of the niter cake to 1 of the ore, and more niter cake is often needed before the fusion is complete. The mass is heated until the fusion is clear, then cooled; the cooled mass is finely ground and then leached with water containing 5 per cent of sulphuric acid. Care must be taken not to heat the solution, as the double sodium zirconium sulphate will be precipitated; this separation, however, depends on the dilution, acidity, and temperature.

TREATMENT WITH HYDROFLUORIC ACID AND FUSION WITH FLUORIDE.

Digestion with hydrofluoric acid was attempted in order to prepare the double sodium or potassium zirconium fluorides directly from the ore. It was not very successful, partly because of the poor recovery of zirconium and the difficulty in recrystallizing these salts

in sufficiently pure condition. One of the methods used for getting the zirconium into solution was to cover the ore with hydrofluoric acid and digest for some time. Sulphuric acid was then added to cover the material, and the solution carried to fumes of sulphuric. The residue was leached in water and filtered from the insolubles; the solution was treated for the recovery of the zirconium as the oxide. The oxide thus obtained was again treated with the hydrofluoric acid and the double fluorides prepared, as will be described later.

The poor recovery by treatment with hydrofluoric acid is attributed by H. C. Meyer^{88a} to the two forms of Zr silicate in the Brazilian zircons. One of these is insoluble in HF. The recovery seldom ran up to 70 per cent of the total ZrO_2 in the material used.

FLUORIDE FUSIONS.

Fluoride fusions with the zirkite ore containing the relatively large amount of impurities or iron and titanium proved to have little advantage. In the preparation of pure salts the fluoride fusions of zirkite were abandoned because iron particularly is difficult to eliminate, and it was found advisable when preparing the pure K_2ZrF_6 to start from relatively pure oxide—99 per cent or better. If zirkite is used, the loss by recrystallization is very great before the salts are free of Fe and Si. However, for other purposes, such as for simply getting the ore soluble in acids, these fusions proved fairly satisfactory but rather expensive.

HEATING WITH LIME AND COKE—VOLATILIZATION OF ZIRCONIUM TETRACHLORIDE.

Attempts were made to get the zirconium into the form of a chloride by heating the ore with a mixture of lime and coke, and later treating the zirconium carbide with chlorine. To convert the zirconium carbide into the chloride with free chlorine requires a high temperature, 400° to 800° C. The chloride distills at about 400° C., but experience has shown that a higher temperature than this is needed to convert satisfactorily the carbide into the chloride; and the great difficulty with this method is in finding suitable apparatus that will withstand the action of chlorine at the high temperature necessary to give a good yield of ZrCl_4 . Also it was found that the carbide is not easily dissolved by dilute acids, and that the solution when formed, if the carbide is treated directly with hydrochloric acid, contains most of the impurities that were in the original ore. Hence there is little to recommend this method of procedure.

Attempts were made to volatilize the zirconium chloride by heating the silicate ore directly with salt and coke. Some zirconium

chloride formed and under certain conditions as much as 50 per cent of the zirconium was distilled as the chloride, but that there was again the difficulty of finding suitable apparatus for this treatment.

HEATING WITH FLUORSPAR AND SULPHURIC ACID.

A new method devised, which was later found to be similar to the method of Glazebrook, Rosenbain, and Rodd^{187a}, was given a great deal of consideration. The method is similar to the original method suggested by Berzelius^d where he volatilizes silicon tetrafluoride from silicates. The equation that was worked out for this reaction may be written as follows:



It was hoped, if this equation properly represented the reaction that would take place, to volatalize the silicon tetrafluoride and perhaps some of the titanium tetrafluoride which has a boiling point of about 284° C. If an excess of sulphuric acid were used, the zirconium would ultimately be obtained in the form of the sulphate. The expectation was this sulphate solution could be diluted and heated to 40° C. and the basic sulphate crystallized directly to yield the pure zirconium basic sulphate. All possible combinations of fluorspar and sulphuric acid with zirkite were tried on a laboratory scale. Extractions were made that yielded 50 to 75 per cent of the total zirconium present in the zirkite ore, but in none was the extraction as high as 100 per cent. After much work, therefore, this method was finally abandoned and for ordinary purposes, digestion with concentrated sulphuric acid alone was found to give about as good results as when used with fluorspar.

SULPHURIC ACID METHOD FOR TREATMENT OF ZIRKITE ORE.

It has long been known that crude oxide of zirconium is rendered soluble in water on prolonged digestion with hot concentrated sulphuric acid. In the main, this has been considered a rather difficult and more or less unsatisfactory treatment of the crude oxide, and has not been advocated strongly. Silicate ores are considered more insoluble than the oxide in sulphuric acid.

Experiments with this method of ore treatment have demonstrated that small quantities of zirkite ore, digested with concentrated sulphuric acid, are often decomposed almost completely. With the larger quantities necessary in working this method on a commercial basis, the recovery ranged from 60 to 95 per cent. This method

^d Berzelius J., Poggendorf's Annalen. 1842, Bd. 1, p. 169.

of ore treatment has been found to be as efficient as any fusion method for rendering zirconium ores soluble. It is simple and it does away with much difficulty in handling solutions that have proved so expensive in fusion methods heretofore advanced. The solution is easily filtered free of silica and contains a minimum of outside impurities like sodium salts, which are introduced in ore treatment by fusion methods.

Zirkite is mixed with four times its weight of sulphuric acid and digested for 1 to 2 hours at a temperature of 400° C. It is then slowly ignited to about 650° C. for 1 hour. This manner of ignition is necessary to remove the last trace of free sulphuric acid. Poor recoveries have been recorded when the material is not ignited to a high enough temperature, no doubt because the presence of free acid lowers the solubility of the neutral sulphate in water or because insoluble basic sulphates of zirconium form. An interesting fact observed in this method of treatment is that, although the iron sulphates present are said to be decomposed at a much lower temperature than 650° C., there is no apparent decomposition of the iron sulphate until the temperature reaches nearly 650° C; then there is appreciable decomposition of the zirconium sulphate as well as of the other sulphates. This overlapping of the decomposition points of the different sulphates precludes selective decomposition of them as was at first hoped.

The effect of different temperatures of ignition and different amounts of water in leaching the sulphates on the percentage of recovery of the zirconium from 10-gram samples of ore can be approximately judged from the following data:

TABLE 8.—*Digestion of zirkite ore with sulphuric acid.*

Temperature of ignition.	Zirconium made soluble.	Volume H ₂ O used for making extraction.
° C.	<i>Per cent.</i>	
400	51	1 to 6.
568	76	
700	50	
450	83	
550	80	1 to 15.
600	86	
650	100	
400	79	1 to 30.
537	81	
600	81	
650	77	1 to 50.
730	61	
780	31.8	
550	100	
650	100	1 to 125.
870	Decomposed with practically no extraction.	

Table 8 shows that in general the extraction per cent of zirconium increases with the temperature of ignition up to about 650° C., and

for the same temperature of ignition the amount of zirconium going into solution increases with the volume of water used in the extraction.

On applying this manner of ore treatment on a larger scale, the recoveries decreased somewhat. Occasionally a recovery as high as 85 per cent was obtained from a large bulk of material, but as a number of factors influence the recovery, it was thought that by properly controlling these, good extraction could be made on a commercial scale.

TABLE 9.—*Recovery of zirconium from zirkite ore—digestion with sulphuric acid.*

Volume of water used for making extraction, 1 to 125.]

Weight of zirkite.	Weight of acid.	Recovery of Zr.
<i>Grams.</i>	<i>Grams.</i>	<i>Per cent.</i>
10	40	90
25	200	80
453	1,812	a 60

^a On heating this material some of the zirkite in the bottom of the dish became caked. Had this been broken up before completing the digestion, the yield would have been much larger, possibly 80 per cent. When the digestion is complete and all the fumes of sulphuric acid driven off, the material remaining should be a very fine grayish white powder.

Numerous trials, 10 to 25 gram samples of zirkite with different ratios of acid to ore being used, showed that a 4 to 1 ratio of acid-ore was just as efficient as higher ratios. On a commercial scale the percentage of recovery of the zirconium can be increased by prolonging the period of digestion. To do this it may be necessary either to increase the ratio of the acid to the ore, or to conduct the digestion in some sort of a receptacle that will retain the acid, such as a reflux condenser or a chamber.

CHAPTER X.—PREPARATION OF PURE ZIRCONIUM COMPOUNDS.

Pure zirconium compounds were prepared, as has been stated before, because they could not be obtained in the market. In the work on the preparation of the metal, the potassium-zirconium double fluoride was used almost exclusively. In order to obtain this salt in a sufficiently pure condition for experiments on the preparation of the metal, it was necessary to start from the relatively pure oxide of zirconium. At first it was not proposed to make any special attempt to prepare a complete series of experimental data on this phase of the subject. However, as the work has been done and was a part of the investigation, it is included in detail.

All of the known methods of preparing zirconium oxide were investigated. For the purpose of comparison, an approximate estimate of the costs for materials entering into each process is appended. The more important methods of purification are described in the following order:

Basic sulphate crystallization.

Oxychloride crystallization.

Precipitation with SO_2 or $\text{Na}_2\text{S}_2\text{O}_3$.

Precipitation as the phosphate and subsequent treatment.

Preparation of the K_2ZrF_6 from the nearly pure oxide.

Miscellaneous methods used in the preparation of ZrO_2 .

1. Sodium carbonate method.

2. Precipitation of crude oxide with ammonia.

3. Criticism of Loveman's method for preparing ZrO_2 .

BASIC SULPHATE CRYSTALLIZATION.

The preparation of zirconium oxide by this method has yielded very satisfactory results. By way of preface to a discussion of the method the following outline of the chemistry of zirconium in sulphate solutions is presented.

It has long been known that zirconium in sulphate solutions forms a number of complexes where existence has been demonstrated by various conductivity measurements and by the action of zirconium sulphate solutions toward various precipitants. In general, the sulphate solutions of zirconium react toward precipitants quite differently from the chloride or nitrate solutions. For example, in nitrate or chloride solutions the precipitation with oxalic acid takes place readily; in solutions of the sulphate there is no precipitation, or at most a gradual one. The complexes of zirconium in sulphate solution have received much attention, and there are numerous references

in the literature to them. In general, it is assumed that variations in temperature, acidity, dilution, and the presence of other soluble sulphates affect or modify the neutral sulphate $\text{Zr}(\text{SO}_4)_2$ to give rise to the various complexes (acidic, basic, and double sulphates).

The most commonly known sulphate of zirconium is the neutral sulphate $\text{Zr}(\text{SO}_4)_2$, which is formed when the oxide or hydroxide is dissolved in concentrated sulphuric acid and the sulphate solution is carried to complete dryness and freedom from sulphuric acid by prolonged ignition to 400°C . The formula of the so-called "neutral" sulphate obtained from aqueous solutions is sometimes written: $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, or $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.

Hauser²⁰⁰ has isolated a basic sulphate ($4\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 14\text{H}_2\text{O}$) from solutions of the "neutral" sulphate in water. This basic sulphate separates out on long standing from solutions diluted to the ratio of 15 parts of water to 1 part of the "neutral" sulphate, when the temperature of the solution is maintained at 39.5°C . Hauser claims that in this separation of the basic sulphate a very pure product of constant composition may be obtained. It is suggested that this salt be used in atomic-weight determinations.

From a study of the sulphate solutions of zirconium, the following factors were determined as being those controlling the crystallization of the basic sulphate, $4\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 14\text{H}_2\text{O}$, from solutions such as will be obtained from the sulphuric-acid digestion of zirkite ore:

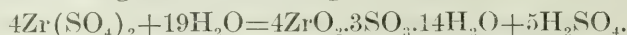
1. A sulphate solution practically free from the sulphates of Na, K, and Ca.
2. An initial acidity of about 0.5 per cent and a maximum acidity (for the basic sulphate to separate) of not more than 3.5 per cent acidity.
3. Sufficient dilution.
4. Proper temperature control.

To obtain a solution conforming to the first condition, the sulphuric-acid digestion of the zirkite ore was developed as described in the previous chapter. To conform with the second, the temperature of ignition of the sulphate was investigated. The dilution necessary was found to vary within wide limits between 30 to 1 to 200 to 1. The temperature has been determined by Hauser for crystallization of the basic sulphate to be about 39.5°C , as previously stated.

The general mode of procedure used in producing the basic sulphate was to leach the ignited sulphate material with the quantity of water necessary to give approximately more than 30 to 1 dilution and less than 40 to 1. After standing for 24 hours the solution was diluted to approximately 50 to 1. The proper amount of water to be added was determined by analyzing the solution for $\text{Zr}(\text{SO}_4)_2$. A

greater dilution was needed when working with the sulphates prepared from zirkite than with purified sulphates.

It is not certain to just what extent the iron and titanium sulphate impurities retard this crystallization. It was observed, however, that while pure solutions of the "neutral" sulphate crystallize readily at a dilution ratio of 15 to 1, solutions of zirkite obtained from the digestion of the ore in sulphuric acid do not crystallize under a dilution of 30 to 1, and are best at dilutions of 50 to 1. Again when zircons, which contain a higher percentage of iron and titanium than the zirkite material, are treated in the same manner as zirkite solutions, there is no crystallization effected at a dilution lower than 80 to 1. During the acid treatment acid sulphates of iron and titanium are formed which increase the initial acidity of the solution, and this greatly retards the hydrolysis. The acidity of the solution during hydrolysis is continually increasing through the production of free acid formed during the separation of the basic sulphate according to the following reaction:



It may be found necessary when this method is tried on a commercial scale to allow more dilution than 50 to 1, to take up the larger amount of free acid that may result from failure to remove free acid during the ignition of larger quantities of zirkite ore.

The table following shows the percentage of zirconium recovered from zirkite by the sulphuric acid digestion and basic sulphate crystallization. Longer standing than three days would yield better results. The data are not as complete or as accurate as desirable because of the difficulty in determining the weights of basic sulphate which were hard to remove from the sides of the test tubes in which they were crystallized.

TABLE 10.—*Recovery of basic sulphate from sulphuric acid digestion of zirkite.*

Temperature ignition.	Weight Zr (SO ₄) ₂ in so- lutions.	Dilution ratio.	Recovery of basic sulphate at end of third day at 39.5° C.
° C.	Grams.		Per cent.
450	0.94	21 to 1	40
470	.94	26 to 1	31
550	.88	22 to 1	36
550	.88	28 to 1	44
550	.88	33 to 1	43.5
550	.88	45 to 1	43
600	.486	40 to 1	39
600	.486	60 to 1	45.5
600	.486	70 to 1	43
600	.486	80 to 1	41
650	.484	41 to 1	58
650	.484	61 to 1	57
650	.484	71 to 1	57
650	.484	82 to 1	58

In all the crystallization experiments the most satisfactory crystallization from every point of view was obtained from concentra-

tions closely approximating or exceeding 50 to 1, and from solutions made from sulphates that had been ignited to 650°C .

The effect of increased temperature would be to hasten hydrolysis. Increased dilution should accomplish the same result. If the solutions are diluted too much, hydrated oxides of zirconium precipitate. It has been observed, however, that when a solution of zirconium sulphate is diluted to perhaps 100 to 1 and allowed to stand at room temperatures a basic sulphate separates out. If this observation is coupled with the idea of Glazebrook, Rosenhain, and Rodd,^{187a} a satisfactory method for preparing chemically pure ZrO_2 directly from zirkite ore can be worked out which does not necessitate maintaining the solution at 39.5°C . for the basic sulphate crystallization.

In this method the ore is treated with 4 parts of concentrated H_2SO_4 , and after the mass is heated dry the temperature is raised to 650°C . After cooling the mass is extracted with 50 parts of cold water, filtered, and sodium carbonate is added to neutralize the free acid formed when the anhydrous "neutral" sulphate changes on going into solution into $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, and also to neutralize the free acid from any acid sulphates not decomposed by ignition. Sodium carbonate is added until a precipitate of zirconium hydroxide just begins to form. The solution is allowed to stand at room temperature for three or four days, and the basic sulphate gradually separates out nearly free of iron, aluminum, and titanium. When this sulphate is filtered, washed, and ignited, a very high-grade zirconium oxide is obtained.

PURITY OF PRODUCT AND FORM OF CRYSTALLIZATION.

Samples of basic sulphate, prepared as described above, proved to be very pure and free from all but the smallest contaminations of iron and titanium. When extreme care was taken to wash the precipitate thoroughly, the impurities of iron and titanium were reduced below a weighable quantity and could be detected only by colorimetry.

The form of the precipitate was determined on a sample that had been dried at 112°C . for several hours and, as will be seen, had evidently lost some water of crystallization.

Weight of BaSO_4 , gram.....	0.0157	Percentage of ZrO_2	54.0
Weight of ZrO_2 , gram.....	.0108	Percentage of H_2O (by diff.)..	19.05
Percentage of SO_3	26.95		

$$\begin{aligned}
 64 - \frac{54}{122.6} &= 0.440; \quad \frac{0.440}{.11} = 4. - \\
 \frac{26.95}{80} &= 0.336; \quad \frac{0.336}{.11} = 3. - \\
 \frac{19.05}{18} &= 1.05; \quad \frac{1.05}{.11} = 9. -
 \end{aligned}$$

which corresponds to the formula: $4\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$.

Other samples which have been ignited to higher temperatures have given the same ratio of ZrO_2 to SO_3 with varying amounts of water.

Production of the oxide from this basic sulphate was affected by ignition to 800°C . to $1,000^\circ \text{C}$., at which temperature the salt is totally decomposed. A typical analysis of the oxide obtained by the crystallization of the basic sulphate and subsequent ignition is as follows:

<i>Analysis of oxide.</i>		Per cent.
SiO_2 -	-----	None.
TiO_2 -	-----	0.06
Fe_2O_3 -	-----	0.10
Al_2O_3 -	-----	Not determined.
ZrO_2 -	-----	99.84

Some of the samples were not as pure as the analysis indicates, but all were pure enough to be an excellent commercial product.

An estimate of the costs for materials for the production of 1 pound of ZrO_2 by the basic sulphate crystallization is as follows:

Cost of producing 1 pound of zirconium oxide.

2 pounds of ore (zirkite), at 6 cents-----	\$0.12
8 pounds of H_2SO_4 , at 1 cent-----	.08
	.20

This cost is exclusive of the cost of labor and equipment, and the calculation is based on a 66 per cent recovery, as basic sulphate, of the amount of ZrO_2 in the ore.

OXYCHLORIDE CRYSTALLIZATION.

Oxychloride crystallization is one of the best-known methods of preparing the pure salts of zirconium, but is much too expensive for use on a commercial scale because of the cost of the concentrated hydrochloric acid used in the crystallizations, as these must be repeated a number of times in preparing the oxychloride from relatively impure materials.

The oxychloride as prepared for this work was obtained from the relatively pure oxide, 95 to 98 per cent ZrO_2 , which was rendered soluble by any expedient means; if any sodium or potassium salts were present, the zirconium hydroxide was first separated by precipitation with ammonia. The precipitated hydroxides when washed free of sodium or potassium salts were collected and dried at 100°C . When dried, they were dissolved in hot concentrated HCl and allowed to crystallize. If the percentage of silica is very high, the

crystallization will be unsatisfactory and the material will have to be carried to dryness on a water bath several times with HCl to dehydrate the silica.

This dried zirconium oxychloride readily dissolves in water, leaving the silica insoluble. The solution is filtered again, evaporated to dryness on the water bath, and taken up with hot concentrated HCl. When the solution cools, the crystals of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ will form and can be recrystallized until pure. The number of recrystallizations necessary depends on the amount of impurities in the original material. In general, 5 to 10 recrystallizations are required. The oxychloride may be ignited directly to the oxide or it may be dissolved in water, the zirconium hydroxide precipitated with ammonia, and the hydroxides ignited to the oxide. Ignition of the oxychloride yields a very hard and granular product; calcining the hydroxide yields the characteristic flour-like oxide.

SODIUM THIOSULPHATE AND SULPHUR DIOXIDE METHODS OF PREPARING ZIRCONIUM DIOXIDE.

The thiosulphate method of precipitating the Zr, Ti, and Th from solution has been given some attention as a means of estimating zirconium in analytical work, and in applying this precipitation to a commercial method for obtaining zirconium compounds free from iron. Contrary to the expressed belief of several authors, this precipitation has proved as complete from a dilute sulphate solution as from a solution of the chlorides. The precipitation of zirconium from sulphate solutions is often hindered or prohibited by the presence of considerable quantities of the sulphates of sodium and potassium. But if a solution of zirconium sulphate, in which there is a relatively small amount of Na or K sulphates, is treated with sodium thiosulphate in considerable excess, the separation will be as good as that made in the chloride solution.

The main factors governing the sodium thiosulphate method of precipitation are as follows:

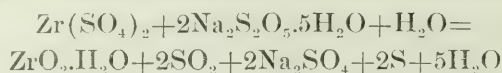
1. The solution must be only very faintly acid, and free from excess of sodium and potassium salts.
2. The solutions should not be concentrated but (about 1 part calculated), ZrO_2 to 50 parts of water.
3. The addition of the thiosulphate should be made at or about 70°C .
4. After precipitation and heating to boiling the solution should be allowed to stand for some time before filtering.

On precipitation with sodium thiosulphate, the solution will first rapidly assume a milky appearance, but on heating near the boiling point will gradually clear up and a flocculent white precipitate will

settle out. In a satisfactory precipitation, the supernatant liquor is clear and the precipitate settles readily. The presence of any considerable amount of sulphur indicates too high an acidity or the presence of certain oxidizing agents.

The sodium thiosulphate precipitation may be as successfully made with samples weighing several pounds as with one-tenth gram samples in the laboratory, but the same precautions as to acidity and dilution and the absence of any considerable amount of sodium and potassium salts must be observed.

After much work had been done on this method of precipitation it was found that very nearly the same method has been patented by Loveman,^{239a} who claims the equation representing the precipitation is as follows:



This equation is not properly balanced, but may approximately represent the reaction.

As the cost of sodium thiosulphate is too high for commercial uses, attempts were made to use SO_2 in place of the thiosulphate. Experiments were conducted to determine the relative efficiencies of thiosulphate and SO_2 precipitations of zirconium from solution. Sodium thiosulphate and SO_2 seem to precipitate the zirconium in the same form and under the same conditions. It was found that the excess of sodium thiosulphate necessary to precipitate the zirconium from a sulphate solution, according to Loveman's patent, was so large that the cost of the precipitant was prohibitory for the production of commercial ZrO_2 , as on such a scale it is often necessary to add a 500 per cent excess of sodium thiosulphate in order to precipitate the zirconium and reduce the iron and other metals. It is estimated that to obtain 1 pound of ZrO_2 by this precipitation requires 20 pounds of $\text{Na}_2\text{S}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, which at 3 cents a pound costs 60 cents. If much iron is present, the consumption is larger. Sulphur dioxide is inexpensive and serves well as a substitute for thiosulphate.

A number of trials were made, using SO_2 . A mixture of 3 pounds of caustic soda and 3 pounds of soda ash was fused in an iron dish and 1 pound of zirkite, 100 mesh, sifted into the fusion slowly so as to avoid the foaming which accompanies this reaction. The mass was fused 1 hour to a clear liquid fusion, after which it was cooled, crushed, and lixiviated three times with hot water. The residue was filtered, washed, and digested with 1:1 HCl , this acid being preferable to sulphuric acid because of the ease with which SO_2 precipitates zirconium from chloride solutions. The solution was filtered, diluted

to a volume of 15 gallons, and heated to boiling; then SO_2 was run in for a short time, only one-fourth of the theoretical amount of SO_2 being required for this precipitation. The precipitated zirconium (and titanium) was washed by decantation and easily filtered; after being dried the precipitate was ignited to the oxide.

The separation of zirconium is complete and the recovery obtained by this method depends on the efficiency of the fusion. A 75 per cent recovery was obtained on the above trial of ZrO_2 containing titanium and traces of iron, a fair grade of commercial oxide. The cost of the above procedure, exclusive of labor and equipment, was about as follows:

Cost of materials used to produce 1 pound of zirconium oxide.

Zirkite (1 pound)	\$0. 00
Na_2CO_3 (3 pounds)	. 045
NaOH (3 pounds)	. 075
HCl , about	. 05
SO_2	Very little.
Total	. 22

On a 75 per cent yield from zirkite containing 75 per cent ZrO_2 the cost per pound of the relatively pure oxide obtained by this method is about 40 cents.

PHOSPHATE METHOD FOR THE PRODUCTION OF ZIRCONIUM DIOXIDE.

The phosphate precipitation has been much used for analytical purposes. It forms the basis for Hillebrand's method for estimating zirconium in rocks and minerals, and also the basis for a recent patent by Carney¹⁶². Zirconium phosphate is the only phosphate that will precipitate from an acid solution in the presence of H_2O_2 . Carney, by a slight modification of this principle, precipitate the thorium, zirconium, and ceric cerium phosphates with sodium pyrophosphate.

This precipitate of zirconium phosphate is exceedingly hard to handle because of its flocculence and trouble in filtering and washing it. On a commercial scale quick filtering and thorough removal of impurities by washing are difficult.

The conditions governing this precipitation are, briefly:

1. The acidity of hydrochloric or sulphuric acids may vary from 3 to 20 per cent.
2. The solutions must be very dilute.
3. The presence of H_2O_2 is required to prevent the precipitation of titanium.
4. The precipitation is hastened by heating and mechanical agitation. Most of the chemists who describe the method allow the phosphate precipitate to stand several hours before filtering.

In an attempt to apply the phosphate method of separating zirconium, 10 pounds of niter cake were fused and 1 pound of zirkite, 100-mesh, was sifted into the liquid melt. After fusion for one hour, the cake was cooled, crushed, and extracted with 20 gallons of hot water. The solution was filtered while hot and the zirconium phosphate precipitated with the calculated amount of disodium phosphate. After settling, the supernatant liquor was decanted and the precipitate and remaining liquor pumped into the filter press. After washing, the phosphates were dried and fused with caustic soda, using 3 parts of NaOH to 1 of the phosphate. The fused cake, after cooling, was crushed and leached with hot water, then the residue treated with 1:3 hydrochloric acid, which dissolved out the iron and other impurities and left the hydrated oxide of zirconium in fairly pure condition. The zirconium hydroxide, or oxyhydroxide, was filtered, washed, and dried. The product was nearly white and had a purity of about 98 per cent.

The bisulphate or niter-cake fusion is fairly efficient for American zircons. The recovery of the ZrO_2 from solutions of the bisulphate (or niter-cake) fusions is much more easily effected by the phosphate precipitation, as SO_2 , or thiosulphate precipitations, are incomplete from this solution.

Inasmuch as the titanium content of the American zircons is ordinarily high, varying with the source of supply, the recovery of the titanium may present an attractive problem. The filtrate from the phosphate precipitation can be nearly neutralized and boiled, or the solution can be hydrolized by any convenient means and the titanium recovered as a high-grade product. As an alternative, after the precipitation of Zr by the phosphate in the presence of H_2O_2 , the acid filtrate may be reduced with SO_2 or by other means and the titanium recovered as the phosphate.

An estimation of the costs of this method of production is given below:

Cost of materials for producing 1 pound of zirconium oxide.

Zirkite (1 pound)	\$0.06
Niter cake (10 pounds)	.03
Sodium phosphate (1 pound)	.03
Caustic soda (3 pounds)	.75
HCl (about)	.02
Total	.215

This figure, 21.5 cents, represents the cost, exclusive of labor and equipment, of treating 1 pound of ore. The recovery was between 60 and 70 per cent, and as all of the steps are quantitative, if the fusion is complete, 100 per cent should be recovered. Figuring on a

70 per cent recovery, this method costs about 40 cents a pound of oxide, exclusive of labor and equipment.

PREPARATION OF THE DOUBLE FLUORIDES.

Potassium fluorzirconate was prepared by dissolving zirconium oxide in hydrofluoric acid in lead dishes; the solution was filtered, a rubber funnel being used, and the hot aqueous solution nearly neutralized with a solution of pure potassium hydroxide or pure potassium carbonate. On cooling the solution the fluorzirconate separated out as a heavy white crystalline precipitate. In this method it is essential that the potassium salt used be entirely free from any sodium salts, as the sodium salt will cause the precipitation of the sodium double fluoride, which is relatively insoluble and more flocculent, like hydroxides, and is difficult to filter quickly. After the solution is cold the crystals of K_2ZrF_6 are filtered off, redissolved in hot water containing a little hydrofluoric acid, the solution filtered hot, the rubber funnel being used, into another lead dish and allowed to recrystallize. The crystals thus obtained are recrystallized, 100 c. c. of water being used for every 25 grams of crystals. The solubility of the potassium salt at room temperature is about 1.5 grams in 100 grams of water, but at $100^\circ C$. the solubility is 25 grams in 100 grams. If the solution be cooled to $2^\circ C$. the solubility is only 0.78 gram in 100 grams of water.

The separation from Ti and Fe in this way is very tedious when these impurities are present in any quantity, but when the oxide used is relatively pure (95 to 98 per cent) the separation can be affected by about three crystallizations. Titanium present in any considerable amount is most difficult to separate by this means, as the solubility of the K_2TiF_6 does not differ much from that of the zirconium salt. Marignac^c gives the solubility of the K_2TiF_6 as 0.55 grams at $0^\circ C$. and 1.28 grams in 100 grams of water at $20^\circ C$. An analysis of the product obtained in the crystallization of the potassium fluorzirconate showed 32.10 per cent zirconium. Theoretically the compound K_2ZrF_6 should contain 32 per cent zirconium. One-gram samples did not contain enough iron or titanium to give colorimetric determinations. This material showed a purity of at least 99.99 per cent, and was used in the preparation of the metal.

On the addition of any soluble sodium salt, such as caustic soda, sodium carbonate, or sodium chloride, the sodium salt is separated from a hot solution of the zirconium fluoride in the same way as the potassium salt. Because of the insolubility of the salt (if it is desired pure) it is best prepared by the double decomposition of the potassium salt with sodium chloride. This sodium salt has a solu-

^c Marignac, C., *Recherches sur les combinaisons du niobrium*: Ann. chim. phys. Ser. 4, t. 8, 1866, p. 1.

bility at 18° C. of 0.387 gram in 100 grams of water, and at 100° C. the solubility is but 1.67 grams in 100 grams.

The salt thus prepared can be repeatedly boiled out with hot water, acidified with a few drops of HF, and be obtained relatively free from impurities. However, the Ti and Fe tenaciously cling to this compound.

The ammonium salt is prepared in the same manner as the potassium salt, a hot aqueous solution of the Zr fluoride being precipitated with ammonia or ammonium carbonate. This salt is about as easy to recrystallize as the potassium salt, but it is difficult to prevent the salt from hydrolyzing during recrystallization. Some very pure samples of the ammonium fluorzirconate have been prepared by this method. No glass or porcelain was allowed to touch the fluoride solutions, but all crystallizations were in lead dishes especially prepared for the work. The salts were free from lead.

MISCELLANEOUS METHODS FOR THE PREPARATION OF ZIRCONIUM DIOXIDE. SODIUM CARBONATE SEPARATION.

Another method that has been tested on a laboratory scale for the preparation of zirconium concentrates is described below. As in the sulphur dioxide method, the ore was fused with 3 parts of caustic soda and 3 parts of soda ash. After cooling the mass was crushed, disintegrated with water, filtered, and washed. The residue was digested with concentrated hydrochloric acid and the mass evaporated to dryness to eliminate the silica.

The zirconium chloride was dissolved out of the residue with water, filtered, and heated to boiling; then an excess of sodium carbonate was added. In an excess of this carbonate the iron is precipitated as a basic carbonate, whereas the zirconium, titanium, and aluminum remain in solution. The last three are at first precipitated, but are redissolved on boiling with an excess of the carbonate. The zirconium is said to form the compound $\text{ZrCO}_3 \cdot \text{ZrO}_2 \cdot 8\text{H}_2\text{O}$.

The solution is filtered and the zirconium and titanium precipitated by the addition of caustic soda. If after the zirconium and titanium are filtered off, CO_2 is passed through the filtrate (caustic soda, sodium carbonate solutions), the caustic soda is converted to carbonate, and the solution may be used again. Although the product is not of very high purity, this method affords a convenient means of obtaining zirconium oxide concentrates.

CRUDE OXIDE BY PRECIPITATION WITH AMMONIA.

The following method was used for the preparation of crude mixed oxides of zirconium, iron, aluminum, and titanium for use in the production of ferroalloys:

Twenty pounds of finely ground zirkite were fused with 100 pounds of niter cake. A good clear fusion was obtained which, after cooling, was extracted with water and pumped through a filter press to remove any undissolved residue. The solution was diluted to fill a wooden tank 3 feet deep and 6 feet in diameter, then heated to boiling and made alkaline with ammonia. The iron, zirconium and other hydroxides precipitated were filtered in a filter press. When the cake was dried it still contained 30 per cent of soluble sodium salts which were dissolved (after drying the cake) with hot water and the oxides were again filtered and washed. These oxides contained much iron, most of which came from the niter cake, and about 3 per cent of silica. The silica was removed by heating with a mixture of HF and H_2SO_4 . The yield was 10 pounds of crude oxide, which represents the extraction of about 75 per cent of the zirconium from the ore. The total cost of the materials used is estimated at not more than 15 cents per pound of oxides produced. Caustic soda or soda ash (no excess) may be used in place of ammonia for the precipitation.

CRITICISM OF LOVEMAN'S METHOD OF ORE TREATMENT.

Attempts were also made to use the method of Loveman,²³⁹ selective digestion of the leached soda ash fusion residues, but in the main these attempts were not satisfactory. All the carbonate fusions made according to the directions in his patent specifications were unsatisfactory: the silica was not entirely removed, and the product obtained from digesting in 1:1 HCl solution was very impure.

Experiments were tried embodying Loveman's plan of separating titanium and zirconium by the differences in solubility of the zirconium hydroxide and titanium hydroxide. In each trial, 1 gram of ore was fused with 2 parts of NaOH and 1 part of Na_2CO_3 to make a complete fusion in a platinum crucible. The residue was leached very thoroughly with hot water, filtered, agitated with 100 c. c. of cold dilute acid for half an hour, filtered again and tested for titanium and zirconium. The results of these experiments are as follows: The original samples contained 12 per cent of TiO_2 .

TABLE 11.—Effect of dilute acids on the freshly precipitated hydroxides of titanium and zirconium.

No.	Concentration of acid.	ZrO ₂	TiO ₂
		<i>Per cent.</i>	<i>Per cent.</i>
1	5 per cent H_2SO_4	45	2
2	3 per cent HCl.....	65	
3	0.8 per cent HCl.....	80	Nearly all re- moved.
4	0.3 per cent HCl.....	90	2
5	0.3 per cent H_2SO_4	90	4

As the results show, nearly all of the titanium may be removed by using about 0.5 per cent HCl in the cold. It is difficult to reconcile Loveman's patent with the data given above, unless Loveman dries and ignites his residues before treating with 1:1 HCl; the insolubility of the residue depends upon the degree of heating, and Loveman may have some process not disclosed in his patent. It may be that Loveman's method is based upon selective hydrolysis rather than upon selective solution in dilute acid. Chloride solutions are readily hydrolyzed, but in such hydrolyses the product is always contaminated with titanium.

CHAPTER XI.—METHODS OF ANALYSIS.

COMPARISON OF METHODS OF ORE FUSION.

Experiments were also tried to get the titanium into solution by the action of very dilute acids in the presence of oxidizing agents, such as $K_2Cr_2O_7$, chlorine water, or H_2O_2 . No decidedly beneficial results were obtained by the use of any of the above oxidizing agents. The first difficulty in making analyses of the ore was in obtaining satisfactory fusions. Many of the methods suggested work well for one ore, but are unsatisfactory for another: hence the different fusion agents were compared before methods of analysis were attempted. The most satisfactory of these agents is described and the relative efficiencies of the others are given.

A decidedly convenient method for getting zirconium ores into solution is by fusion with about 3 parts of sodium hydroxide and 1 part of sodium peroxide in a nickel dish. The fusion takes only a low temperature and is completed in a few minutes. Nickel crucibles were used many times for this fusion without much injury. In the analysis of metallic zirconium the metal was usually obtained in solution by long-continued digestion with aqua regia on a hot plate. Any residue remaining after this digestion was made soluble by fusion with potassium or sodium bisulphate. There is some question as to the length of fusion and the temperature, but these have been regulated as far as possible to conform to the procedure usually adopted.

TABLE 12.—*Efficiencies of various fusion agents with zircon.*

Fusion mixture.	Parts fusion mixture to 1 of ore.	Time of fusion.	Undecomposed residue.
Na_2CO_3	5 Na_2CO_3	1 hour.....	50 per cent after second fusion.
KNO_3	1 KNO_3	Digested one-half hour.....	85 per cent.
Concentration of H_2SO_4 at 180-190° C.	10 to 1.....	Digested 5 hours and heated to dryness.	25 per cent.
Concentration of H_2SO_4 at boiling point.	10 to 1.....	Boiled to dryness twice.....	30 per cent.
Concentration of HF.	10 to 1.....	1 hour.....	Incomplete.
$Na_2S_2O_7$ to clear fusion.	3 $NaOH$	20 minutes; temperature of fusion low.	Complete.
$NaOH$ in Na_2O_2	1 Na_2O_2	1 hour.....	Very incomplete.
$NaCl$	10 to 1.....	1 hour.....	10 per cent complete.
Na_2CO_3	2 $NaOH$	1 hour.....	Very high temperature and necessary for good results.
$NaOH$	1 Na_2CO_3	1 hour.....	Complete.
Na_2CO_3	4 Na_2CO_3	1 hour.....	Complete.
$Na_2B_4O_7 \cdot 10H_2O$	1 borax.....	1 hour.....	Complete.
NaF	5 to 1.....	1 hour.....	Complete.

As has been stated, these trials were made with zircon sand which is very resistant toward fusion agents. Zirkite is decomposed much more readily. For example, zircon sand yields a 75 per cent extraction with sulphuric acid, whereas zirkite is completely decomposed when treated in this way.

METHODS OF PRECIPITATION OF ZIRCONIUM.

In one of the first analyses, an attempt was made to determine the zirconium in an ore by the phosphate, sodium thiosulphate, and sodium iodate methods as described in the literature. These analyses, tabulated below, are typical comparisons of the results obtained by the various methods of precipitation; they were all of the same sample of ore:

TABLE 13.—Percentage of ZrO_2 in zirkite by different methods of analysis.

Weight, ore. (aliquot).	Weight, phos- phate.	Weight, ZrO_2 .	Per cent, ZrO_2 .
0.0853	0.1215	0.0626	73.3
.0707	.1010	.0520	73.5
.2000	} Sodium thiosul- phate method.	.1740	87.0
.2000		.1700	85.0
.2000		.0947	47.35
	Sodium iodate pre- cipitation.		

Table 13 shows it would be hard for a novice to decide whether this ore contained 47 per cent ZrO_2 or 87 per cent ZrO_2 . The same kind of results were obtained with other ores and before accurate work could be undertaken, it was necessary to find which method gave the proper results.

The commonly mentioned precipitating agents for zirconium are:

(1) Sodium iodate; (2) sodium thiosulphate or sulphur dioxide; (3) phenylhydrazine; (4) phosphate; (5) cupferron. The results obtained by these precipitants are compared on page 77. The method used in making the precipitation is described in the paragraphs following.

SODIUM IODATE.

The sodium iodate precipitation was made from a solution that had been made alkaline with ammonia and then had enough HCl added to just redissolve the precipitated hydroxides. Sodium iodate solution was added to 50 per cent excess. The total volume of the solution was about 200 c. c. The precipitate was allowed to stand several hours, filtered, washed with cold water, and ignited; then the ZrO_2 was weighed. In some of the later trials the washing was done with 2 per cent sodium iodate solution followed by dilute ammonia.

SODIUM THIOSULPHATE OR SULPHUR DIOXIDE.

The thiosulphate or sulphur dioxide precipitations were made in faintly hydrochloric or sulphuric acid solutions. An excess of 500 per cent of $\text{Na}_2\text{S}_2\text{O}_3$ was found to be necessary to completely precipitate zirconium from sulphate solutions. A 100 per cent excess was used in the chloride solutions. The SO_2 gas is not needed in so large an excess, as this gas seems to promote hydrolysis from hot solutions rapidly. The precipitant was added at temperatures of 70° to 100° C. and to a volume of about 200 c. c. containing about 0.1 gram ZrO_2 . The larger the amount of iron, the larger the dilution that should be used.

The precipitate was washed with hot water, ignited, and weighed as $\text{ZrO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3$.

PHENYLHYDRAZINE.

The phenylhydrazine precipitation was made from a faintly acid solution (HCl) that had been previously reduced with sodium thiosulphate. One to three c. c. of phenylhydrazine was added to a solution of about 100 c. c. containing 0.1 gram ZrO_2 . The precipitate was filtered and washed with water containing a few drops of phenylhydrazine. The precipitate was ignited and weighed as $\text{ZrO}_2 + \text{Al}_2\text{O}_3$.

PHOSPHATE.

Phosphate precipitations were made from solutions of 5 to 20 per cent sulphuric acid according to the amounts of impurities in the solution. A volume of about 200 c. c. was used to 0.1 gram of phosphate precipitate, and only a small excess of the soluble phosphate was used. In making the precipitation the solutions were heated, H_2O_2 added, the phosphate added, and then the solution was allowed to stand at least several hours before filtration. The solutions were filtered, washed with hot water, ignited, and weighed as ZrP_2O_7 . The ZrO_2 was calculated by the factor 0.518. Not more than 0.1 gram of the zirconium phosphate should be precipitated at one time, because of the difficulty in washing and igniting larger quantities.

The percentage of acidity varies with the amount of iron, titanium, and aluminum. Although Hillebrand recommends only 3 per cent sulphuric acid for making this precipitation, good results are obtained from solutions of much stronger acidity. Nicolardot and Regalde³⁷⁶ have recently published a paper on the phosphate method, an abstract of which is given here:

The separation of Zr from Fe, Cr, and Al may be made complete under the conditions as outlined below. The presence of bismuth, which is rarely associated with the Zr, interferes with this separation. These experiments were the result of observation that the method of precipitating the Zr as the phos-

phate were not concordant among the several authors advocating this method. The effect of variation of acidity and foreign elements in the solution was studied. The solution used was one of the nitrate of Zr, which gave on precipitation with ammonia and with sodium thiosulphate the following results:

	ZrO ₂
NH ₄ OH.....	47.8 mg. in 50 c. c.
Thiosulphate.....	48.0 mg. in 50 c. c.

In making the determination 50 c. c. of this solution was taken, to which, after making the required acidity, was added an excess of (NH₄)₂HPO₄ (10 c. c. of solution made from dissolving 10 grams of the salt in 100 c. c.). After standing for two hours, a gelatinous precipitate is obtained which filters with difficulty. The precipitate is allowed to stand until all trace of the Zr precipitate is out of the solution, and then is decanted in the case of higher acidities and filtered after dilution with water. The precipitate, after thorough washing, is calcined to constant weight. The factor for ZrO₂ is found to be 0.487. The factor used by Treadwell is 0.50 and by Hillebrand is 0.518. The factor for Zr is 0.36.

To determine the effect of acidity a pure solution of Zr was used containing 0.0487 grams.

TABLE 14.—Effect of H₂SO₄ on the precipitation of Zr phosphate.

Parts H ₂ SO ₄ per 100 c. c.	Weight of phosphate.	Factor	ZrO ₂ re- covered.
Neutral.	0.0980	0.487	0.478
1	.0975	.487	
3	.0975		
5	.0980		
10	.0970		
20	.0970		
35	.0950		
50	.0900	.487	Loss.

It is to be seen that up to an acidity of 20 per cent the precipitation is still complete and that more than this amount can not be used. In the precipitation the ammonium phosphate is preferred in the place of the alkali phosphates.

Separation of Fe, Cr, and Al.

The solution used was the same as previously used, containing 0.0478 grams ZrO₂.

TABLE 15.—Effect of impurities on Zr phosphate precipitation.

Acidity.	Weight of phosphate in presence of—		
	Fe.	Cr.	Al.
Neutral.	0.170		
1	.136	0.104	0.1100
5	.114	.104	.0990
10	.106	.104	.0980
15	.103		.0980
20	.0980	.098	.0975

With Fe and Cr the precipitates on calcination showed more or less color, which was directly proportional to the degree of acidity. At 20 per cent acidity the precipitate ignited to white. The separation from Al can be made in an acidity of 10 per cent.

TABLE 16.—*Exact conditions of acidity for complete separation from Fe.*

Acidity, per cent.	Weight of phosphate.
16	0.103
17	.103
18	.102
19	.100
20	.098

The Zr may be separated from Fe when the acidity is at least 20 per cent. Trials using the acidities suggested by Treadwell and Hillebrand (1 per cent) and heating the solution for some time yielded poor results. Duplication of the same and letting stand for 24 hours before filtering gave an unsatisfactory separation.

The precipitation of Zr as the phosphate from an acidic solution must take place from an acidity of 20 per cent to free completely the Zr from Fe. The solution after precipitation must be allowed to stand for several hours until the precipitate is entirely settled and the strong acid solution decanted. The precipitate is then washed with water and filtered on paper and ignited.

Since this work was done, Lundell and Knowles³⁷² have recommended the following conditions for the precipitation of zirconium phosphate:

Volume of solution.—From 25 c. c. for small amounts (0.005 gram ZrO_2) to 200 c. c. for larger amounts (0.19 gram ZrO_2).

Acidity.—20 per cent sulphuric acid.

Hydrogen peroxide.—10 c. c. do no harm.

Precipitant.—Secondary ammonium phosphate in excess (10 to 100 times the theoretical requirement).

Precipitating conditions.—(1) Temperature: Cold or 40 to 50° C. (2) Time: Two hours for amounts larger than 0.005 gram; six hours for smaller quantities.

Filtration.—Warm, decant, and wash in beaker.

Washing.—Cold 5 per cent NH_4NO_3 solution.

Ignition.—Over low flame until carbon is destroyed, followed by blasting.

These authors have shown that under these conditions the zirconium phosphate is precipitated completely and quantitatively separated from iron, aluminum, chromium, titanium, cerium, and thorium.

CUPFERRON.

The cupferron precipitation was made according to the directions of Baudisch and King;^{342a} an extract of their paper follows:

Cupferron is prepared by dissolving Beta-phenylhydroxylamine in ether at 0°C., passing in dry ammonia, and adding excess of amyl nitrite, when a snow-white crystalline mass of ammonium nitrosophenylhydroxylamine is formed.

Cupferron is used in quantitative analysis for separating copper and iron from most of the metals. The iron and copper are precipitated in strongly acid solution with cupferron, the precipitate filtered, washed with water, and finally

with ammonium hydroxide. The latter dissolves the copper, but not the ferric salt. The ferric salt is soluble in chloroform, ether, acetone, etc., and may be dissolved and separated from other salts, such as those of lead, silver, or tin, which may have been precipitated with it. (Baudisch, *Chem. Ztg.* 1909, Jahrg. 33, p. 1298; Blitz and Hodtke, *Ztschr. anorg. Chem.* 1910, Bd. 55, p. 426; Hamus and Soukup, *Ztschr. anorg. chem.* 1910, Bd. 68, p. 52; Frenzenius *Ztschr. anal. Chem.* 1911, Jahrg. 50, p. 35). The use of cupferron as an analytical reagent is limited by virtue of its explosive properties.

Under the name of "cupferron" one of us (Baudisch) introduced the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5(NO)ONH_4$, into quantitative analysis as a precipitant for cupric and ferric ions. By means of cupferron, iron and copper may be separated very rapidly and exactly, not only from one another but also from almost all other metals. The new method exceeds in elegance, simplicity, and rapidity of operation all the methods known up to the present time for the separation of iron and copper, and has already met great favor in technical analysis in factories and in mining and metallurgical plants.

The advantages of precipitating with cupferron are as follows:

1. The iron and copper are precipitated from solutions strongly acid either with mineral or acetic acids. The precipitated iron and copper salts may be very easily and thoroughly washed free from the chlorides, nitrates, sulphates, etc., of any other metals which may be in solution.

2. The precipitates settle rapidly and may be filtered off without loss of time.

3. The separation of the iron from the copper is accomplished simply by washing the precipitate with dilute ammonium chloride on the filter paper. The ferric salt is completely insoluble and remains on the filter.

4. The iron salt is readily soluble in ether, chloroform, acetone, etc., and may be dissolved on the filter, away from any other metallic salts such as lead, silver, tin, mercury salts, which may have been simultaneously precipitated.

The particular value of the new method lies in the fact that by its means iron may be rapidly separated from aluminum, manganese, chromium, nickel, and cobalt. The "cupferron" method has been thoroughly tested from many sides and the work of H. Nissenson, A. Blitz, O. Hodtke, and Frenzenius quite confirm our results.

Cupferron will undoubtedly find extensive application in the quantitative analysis of widely different material, for it has also been discovered that titanium, cerium, and zirconium may be quantitatively precipitated from acid solutions by it.

An example showing the application of the method to a manganese ore may be of value.

Dissolve 5 grams of finely divided ore in 60 c. c. of concentrated HCl, oxidize the iron with $KClO_3$, and after expelling the chlorine, dilute to 500 c. c. with water. Pipette out 25 c. c. into a beaker and add 20 c. c. of concentrated HCl and 100 c. c. of cold, distilled water. Allow a solution of about 3 grams of cupferron in 50 c. c. of cold water to flow in a fine stream down the side of the beaker, with constant stirring. A brownish-red, partly amorphous, partly crystalline precipitate separates out. As soon as a drop of the reagent causes the formation of a snow-white crystalline precipitate all the iron is down. For certainty's sake add an excess of the reagent, stir well, and filter off with suction. In case the last particles of the precipitate cling tenaciously to the beaker add a little ether to loosen them, and then remove the ether by adding a little boiling water. In this manner it is possible to quantitatively transfer the precipitate to the filter. The precipitate is now washed with cold water until the filtrate is no longer acid with the mineral acid used. Manganese may be

determined in the filtrate. The precipitate is now washed twice with dilute ammonia (1 volume concentrated NH_4OH to 1 volume H_2O) in order to remove the excess of reagent. Wash once more with cold water and fold the wet paper and precipitate together and dry in a weighed platinum or porcelain crucible with a small flame. Then cover the crucible and heat until no more inflammable gases are evolved and then ignite to Fe_2O_3 , cool and weigh.

1. Substance 5.0 grams $\frac{25}{500} = \frac{1}{20}$ taken Fe_2O_3 0.0330 = 13.2 per cent.

2. Substance 5.0 grams $\frac{25}{500} = \frac{1}{20}$ taken Fe_2O_3 0.0331 = 13.2 per cent.

The analysis requires about $1\frac{1}{4}$ hours, but without inconvenience a number may be simultaneously carried out.

PREPARATION OF CUPFERRON.

Sixty grams of nitrobenzol, 1,000 c. c. of distilled water, and 30 grams of ammonium chloride are thoroughly stirred up in a wide-mouthed bottle with an efficient stirring apparatus until a milky emulsion is formed. Into this emulsion (constant stirring) add 80 grams of zinc dust (the amount depends on the quality) in very small portions at a time. During the addition of the zinc dust the temperature must be kept between 15° and 18° C. This may be accomplished by simply throwing pieces of ice into the rapidly whirling liquor from time to time. Continued vigorous stirring and keeping the temperature within the prescribed limits are the essentials which determine a good yield. The reduction is continued until the odor of nitrobenzol vanishes. The time required for the reduction depends on the value of the zinc dust. It usually takes half an hour to reduce 60 grams of nitrobenzol. The white zinc hydroxide is now filtered off with suction and the filtrate cooled to 0° C. with ice, and NaCl is added to saturation. In a little while a thick mass of snow-white crystals forms. Filter off right away with suction and dry between filter paper. The yield of phenylhydroxylamine is usually about 70 to 85 per cent of the theoretical. As phenylhydroxylamine solutions are vigorous skin poisons and may pass through the unbroken skin into the blood, the hands should be washed with water and alcohol in case they come in contact with such solutions.

The freshly prepared phenylhydroxylamine is dried for an hour between filter paper and then dissolved in 300 to 500 c. c. of commercial ether. The ether solution is filtered through a dry filter and cooled to 0° C. Into this cold solution dry ammonia gas is passed for about 10 minutes and then add somewhat more than the theoretical amount (more than 1 mol.) of fresh amyl nitrite all at once. The clear solution will suddenly get hot and the entire vessel will be filled with snow-white crystals of the ammonium salt of nitrosophenylhydroxylamine.

The brilliant snow-white crystals are filtered off with suction, washed with ether, and dried between filter paper. They are then to be placed in a well-closed bottle with a piece of solid ammonium carbonate.

The salt prepared in this manner and thus preserved will be found a welcome and thoroughly satisfactory precipitating and separating agent for copper and iron in any busy laboratory.

COMPARISON OF METHODS.

The several methods of precipitation were tried with various solutions, some of them pure and others containing iron, aluminium, and titanium. The results of these trials are shown in the tables below. The first table shows the weights obtained by using 50

c. c. of a sulphate solution prepared directly from zirkite ore. The quantity of zirconium should be the same in all tests.

TABLE 17.—Weight ZrO_2 found in 50 c. c. of a given solution by different methods.

			ZrO ₂ by difference.
Phosphate method (51.8 per cent for ZrO₂).			
Weight of phosphate.	Weight of ZrO ₂ .	Average.	
0.2414	0.1250	0.1257	
.2443	.1265		
Sodium thiosulphate method (ZrO₂ and TiO₂).			
Weight of ignited precipitate.		Average.	
0.1699		0.1699	
Sodium iodate precipitate.		Average.	
0.0634		0.0588	
.0542			
Total hydroxides by precipitation with NH ₄ OH, ZrO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , TiO ₂ .		Average.	0.1246
0.1949		0.1925	
.1910			
.1921			
Total hydroxides by precipitation with KOH.		Average.	
0.2167		0.2242	
.2318			
Fe ₂ O ₃ by H ₂ S precipitation in ammonium tartrate solution.		Average.	
0.0441		0.0440	
.0439			
TiO ₂ colorimetrically.....			.0039
Al ₂ O ₃ by difference.....			.0200

The results of the KOH precipitation are too high and those with sodium iodate too low. When the weights of Al₂O₃, Fe₂O₃, and TiO₂ are subtracted from the weight of the total hydroxides, the value remaining, representing the weight of ZrO₂, checks closely the value obtained by the phosphate method.

Total hydroxides by ammonia, 0.1925.

This represents the weight of Al₂O₃, Fe₂O₃, TiO₂ and ZrO₂ = 0.1925 - (Al₂O₃, 0.0200 + Fe₂O₃, 0.0440 + TiO₂, 0.0039) = 0.1246.

ZrO₂ by phosphate = 0.1257.

The sodium thiosulphate results are too high. The phosphate method seems to give good results. It is difficult to see how the zirconium could be precipitated free of aluminum by the sodium thiosulphate method, as stated by some authors, as this same procedure has been suggested for the precipitation of alumina.

A series of experiments were made on the precipitation of zirconium phosphate with different quantities of zirconium in solution, in order to see whether the quantity of zirconium greatly affected the checking of duplicate experiments.

TABLE 18.—*Effects of checking duplicate determinations with different quantities of phosphate.*Phosphate (Na_2HPO_4); 10 per cent H_2SO_4 .

Weight of phosphate.	Weight of ZrO_2 (factor .518).	Average weight.
0.1545	0.0800	} 0.0782
.1477	.0765	
.0989	.0513	} .0496
.0935	.0479	
.0383	.0204	} .0204
.0386	.0205	
.0382	.0203	

The above data show that fairly good checks can be obtained by this method of precipitation if the quantity of phosphate is small. With more than 0.1 gram of phosphate, proper washing of the precipitate is difficult, as is proper burning to a white residue.

When the phosphate is fused with NaOH and the ZrO_2 is obtained thus, larger quantities of phosphate can be taken.

Weight of phosphate.	Weight of ZrO_2 .	Average.
Not taken.	0.2414	} 0.2429
	0.2443	

Tests to show the effect of using different phosphates gave the same results with ammonium as with sodium phosphate.

TABLE 19.—*Effect of using different soluble phosphates for precipitation.*

$(\text{NH}_4)_2\text{PO}_4$ Weight of phosphate.	5.5 per cent H_2SO_4 . Weight of ZrO_2 .	Average.
0.1495	0.0744	} 0.0756
.1427	.0739	
Na_3PO_4 :		} .0731
0.1358	.0705	
.1420	.0735	
.1408	.0730	
.1417	.0734	} .0747
H_3PO_4 :		
0.1400	.0726	
.1482	.0768	

Trials of the sodium thiosulphate method of precipitating zirconium from pure zirconium solutions were tried first, with the results shown in Table 20.

TABLE 20.—*Thiosulphate precipitation from pure sulphate solutions.*

	Weight of ZrO_2 (grams).	Average weight (grams).
Precipitation with NH_4OH	0.0865	} 0.0865
	.0865	
Precipitation with $\text{Na}_2\text{S}_2\text{O}_3$ using 250 c. c. of solution and 5 c. c. saturated solution $\text{Na}_2\text{S}_2\text{O}_3$	.0845	} .0841
	.0838	
Using 10 c. c. saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution	.0845	} .0847
	.0850	
Using 15 c. c. saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution	.0851	} .0859
	.0866	

Table 20 shows that from pure solutions made faintly acid with HCl or H_2SO_4 zirconium can be precipitated with sodium thiosulphate with a high degree of accuracy. In the presence of large amounts of iron, aluminum, and titanium, the results are not consistent.

TABLE 21.—*Precipitation with thiosulphate in the presence of impurities.*

	Weight of oxides.	Remarks.
Effect of presence of aluminum on thiosulphate precipitation of zirconium; solution containing 0.0865 grams ZrO_2 and 0.0643 Al_2O_3 .	0.1136	{ Aluminum precipitated partly but not completely.
	.1248	
	.0643	{ Aluminum by itself is completely precipitated with $\text{Na}_2\text{S}_2\text{O}_3$.
	.0643	
Although iron is not precipitated with sodium thiosulphate, the results below do not agree in any respect: Using 0.0865 grams ZrO_2 ; 0.0643 grams Al_2O_3 and 0.1514 Fe_2O_3 ; (Na_2SO_4 present).	.0988	{ Precipitate carried all of the zirconium and varying amounts of aluminum.
	.1873	

The results from the use of phenylhydrazine for precipitating zirconium are given below. The solution contained 0.0498 grams ZrO_2 by the phosphate method. Weight of ZrO_2 by phenylhydrazine method, 0.0487 and 0.0470.

Phenylhydrazine throws down the aluminum as well as the zirconium. The precipitate is hard to wash and slow to filter.

Phenylhydrazine was also compared with cupferron as a precipitating agent. These weights of materials were taken for analysis: ZrO_2 , 0.0860 grams; Fe_2O_3 , 0.0357 grams; Al_2O_3 , 0.0471 grams. The results by the phenylhydrazine method are as follows: Phenylhydrazine, 0.1388 and 0.1373; average, 0.1380.

The weight of oxides obtained by the phenylhydrazine precipitation very nearly equals the sum of the weights of Al_2O_3 , and ZrO_2 , in the solution ($0.0860 + 0.0471 = 0.1331$). Some iron was in the phenylhydrazine precipitate, probably from failure to wash the precipitate clean on the filter paper.

The cupferron precipitation was made from the same solution. Weight of cupferron precipitate ignited as $\text{ZrO}_2 + \text{Fe}_2\text{O}_3$, 0.1213, 0.1219, and 0.1213; average, 0.1215.

The sum of weights of ZrO_2 and Fe_2O_3 ($0.0860 + 0.0357$) equals 0.1217. The separation from aluminum was very exact. The precipitate is easy to filter and wash.

Credit is due to L. W. Dunham for valuable aid in making some of the analyses listed above.

CONCLUSIONS.

The following general conclusions may be made regarding the various methods of precipitation of zirconium:

1. The sodium iodate results are always too low, probably because of the comparatively high solubility of the salt in dilute acid. It can be used only with special precautions for accurate quantitative work.

2. Sodium thiosulphate gives good results in pure solutions, but can not be used with success in solutions containing much Na_2SO_4 , iron, aluminum, etc. It takes a 100 per cent excess of $\text{Na}_2\text{S}_2\text{O}_3$ in chloride solution and a 500 per cent excess in sulphate solutions for complete precipitation.

3. Phenylhydrazine gives fairly good results, but the precipitate is slimy and is hard to filter and wash.

4. The phosphate precipitate can be checked successfully if the quantity of precipitate does not exceed 0.1 gram. Larger quantities can not well be washed free of impurities $(\text{NH}_4)_2\text{HPO}_4$, Na_2HPO_4 , or H_3PO_4 give equally good results. When a large quantity of phosphate is precipitated, it should be ignited, fused with NaOH and the zirconium weighed as oxide.

5. Cupferron is the only reagent that quantitatively separates zirconium and aluminum. The cupferron precipitate is easy to handle and precipitates zirconium and iron from solutions with great accuracy.

METHODS OF ANALYSIS.

As much trouble was experienced in trying to precipitate zirconium by itself with sodium thiosulphate, sodium iodate, etc., special methods are needed to make accurate analyses of zirconium ores and impure metal. In analyzing ores, 1 gram of ore is fused with NaOH and Na_2O_2 as already described. The fused mass is readily dissolved away from the crucible by boiling with water; the solution is filtered and the residue thoroughly washed. The filtrate contains the excess caustic soda, sodium aluminate, and a part of the silica as sodium silicate; whereas the residue contains the remainder of the silica, the iron as ferric oxide, sodium zirconate and sodium titanite. The silica is collected from the filtrate by making the solution acid with H_2SO_4 and evaporating to fumes of sulphuric acid. The silica is filtered from the diluted solution, and the filtrate placed in a 1,000-c. c. volumetric flask for future use. The silica is separated from the residue by treating the latter with 10 per cent H_2SO_4 to dissolve the iron, zirconium, and titanium and evaporating to fumes. After dilution, the silica from this solution is filtered off and washed on the same paper as previously used. The filtrate is added to that in the volumetric flask.

The paper containing the silica is ignited, weighed, and treated with H_2SO_4 and HF to volatilize the silica. The residue is again weighed and the silica obtained by loss in weight. There is usually some residue of ZrO_2 and TiO_2 which is not volatile with HF ; this is fused with potassium bisulphate and dissolved in water, and the filtrate is added to the filtrates in the volumetric flask. The combined filtrates now contain all of the Zr , Ti , Al , and Fe and are made up to 1,000 c. c. in the flask, the solution being kept about 5 per cent acid with H_2SO_4 .

The method as outlined consists in weighing the total hydroxides precipitated by ammonia, determining the zirconium, iron, and titanium on separate portions, and finding the aluminum by difference. Zirconium hydroxide or phosphate is difficult to wash and handle, so it is preferable to work with very small quantities rather than take time in washing the precipitate clean.

Two 100-c. c. portions of the solution are made alkaline with ammonia, the solution is boiled and allowed to stand; then the total hydroxides filtered and washed in the same way as aluminum hydroxide is handled. On ignition this gives the weights of the mixed oxides of ZrO_2 , TiO_2 , Fe_2O_3 , and Al_2O_3 .

Two 100-c. c. portions that are 5 per cent acid with H_2SO_4 are treated with a few cubic centimeters of hydrogen peroxide solution and a slight excess of $(\text{NH}_4)_2\text{HPO}_4$ or Na_2HPO_4 ; the solution is heated gently to boiling and allowed to stand. It is assumed that the zirconium precipitates under these conditions as, perhaps, an acid phosphate which, when ignited, yields the pyrophosphate (ZrP_2O_7). If the pyrophosphate is obtained on ignition, 51.8 per cent of the weight obtained should give the weight of ZrO_2 . Most authors agree that if 51.8 per cent of the weight of phosphate is taken the results for ZrO_2 are too high. This may be due to the phosphate not having a constant composition, but the great difficulty in washing the precipitate may have much effect on the weight of the phosphate.

For accurate work, therefore, the zirconium phosphate has not been weighed directly. The phosphate precipitate has been thoroughly washed, ignited, the residue fused with sodium carbonate in a platinum crucible, and the fused mass extracted with water and filtered. The phosphoric acid is thus removed in the filtrate, the zirconium remaining as the insoluble zirconate. After thorough washing, the paper and contents are ignited and fused in bisulphate. The zirconium sulphate is dissolved in water and precipitated as the hydroxide with ammonia. The $\text{Zr}(\text{OH})_4$ is filtered, washed, ignited, and the ZrO_2 weighed. If much titanium is present, the phosphate must be reprecipitated to get it pure.

The iron is determined by precipitation as a sulphide. To each of two 100-c. c. portions of the original solution 0.5 grams of tartaric acid is added and the solutions are heated to boiling; then the solutions are made alkaline with NH_4OH and the H_2S added slowly for about 10 minutes. The iron is precipitated as the sulphide which is filtered off, washed, ignited, and weighed as Fe_2O_3 . It has been found that the weight of this precipitate is sometimes too high and the iron should be titrated with permanganate for accurate results. The titanium may also be determined on a separate portion of the solution by Weller's method with hydrogen peroxide.

The aluminum oxide was found by subtracting the weights of the ZrO_2 , TiO_2 , and Fe_2O_3 from the weight of total hydroxides. The separation of the aluminum is rather difficult, and sometimes the exact content, if small, of aluminum oxide in the ores is of little importance. The aluminum has been determined by precipitating the Zr, Ti, and Fe with strong KOH, diluting the solution, filtering, making the solution acid with HNO_3 and alkaline with NH_4OH . This precipitates the aluminum hydroxide, which is filtered, ignited, and weighed. Experience has shown that too high results are always obtained by this method, and it is preferable to find the aluminum by difference.

Separate portions of the solutions are taken in practically every case to avoid tedious separations. If the phosphate determination is used the precipitation of the total hydroxides is included simply to serve as a check on the results of the separate determinations.

In making analyses of solutions containing a large proportion of impurities, the greatest difficulty is in separating zirconium and aluminum. All of the methods now suggested in the literature were tried and compared during the progress of the work, the cupferron method proving to be the only one by which aluminum and zirconium can be accurately separated.

In making an analysis by the cupferron method, the solution is prepared as given in the previous outline. Two 100-c. c. portions of the solution are made 10 per cent acid with sulphuric acid and a solution containing 3 grams of cupferron reagent is added. After standing over night the solution is filtered and the precipitate which contains all the iron titanium and zirconium, without any aluminum, is thoroughly washed with cold water. It can be ignited and then weighed as combined oxides. The aluminum is determined by making the filtrate alkaline with ammonia, filtering, washing, igniting, and weighing as Al_2O_3 . The iron and titanium are determined from separate portions as described in the previous scheme of analysis. The only drawback to this method is the difficulty in preparing the cupferron reagent, as already described in the abstract by Baudisch and King^{342a}.

CHAPTER XII.—EXPERIMENTAL WORK ON AMORPHOUS ZIRCONIUM.

REVIEW OF METHODS OF PREPARATION.

In Part I of this bulletin it was stated that various authors claim the existence of at least four varieties of zirconium metal—amorphous, crystalline, graphitoidal, and sintered.

The so-called crystalline zirconium heretofore prepared has been shown by Weiss and Neumann, Wedekind, and others to be an alloy of zirconium and aluminum. The graphitoidal form is described by only one or two authors, and Wedekind questions its existence; possibly it may be partly sintered, amorphous zirconium. Attempts to prepare graphitoidal zirconium in the course of the present work were unsuccessful.

Many authors have prepared the amorphous metal of 49 to 98 per cent purity, and some of its properties are fairly well described. There is, however, much discrepancy regarding this best-known variety. For example, the specific gravities given range from less than 4 to more than 6. The melting point has been given as low as $1,300^{\circ}$ C. and as high as $2,350^{\circ}$ C. Not only do these discrepancies apply to one variety of the metal, such as the amorphous, but the same figures are given for the sintered metal as well as for the crystalline. One writer says that the melting point of sintered metal is above $1,500^{\circ}$ C., but also says that the amorphous is sintered at $1,000^{\circ}$ C. Sintering must represent at least a partial fusion; and if the above statement be true, the metal must be very impure.

One author says that crystalline zirconium is prepared by the electrolysis of the fused fluorides, while another claims this method yields amorphous metal. Troost claims to have prepared crystalline zirconium by reducing sodium zirconate with iron at the melting point of copper. In general, it does not seem possible that any of the varieties of zirconium could be prepared in this way.

The general plan the authors followed in this part of the investigation was to duplicate as far as possible the work of previous investigation, to analyze the products thus obtained, and to introduce modifications of the existing methods or to develop new ones if possible. Each variety of metal was treated separately, although it is difficult to separate the amorphous and sintered metal; and also to distinguish between the so-called crystalline and the zirconium-aluminum alloys.

In the present work the term "coherent" has been introduced to distinguish the truly solid white metal, resembling white steel in appearance and hardness, from the partly fused metal which Wedekind has called sintered zirconium.

From the literature on zirconium the following methods for preparing the amorphous metal were obtained:

1. Berzelius³⁹⁸. Reduction of K_2ZrF_6 (by heating to red heat) with potassium in an iron dish.
2. Troost⁴²². Passing $ZrCl_4$ vapors over heated sodium.
3. Phipson⁴¹⁶ and also Winkler⁴⁴². Heating zirconia with magnesium or zinc in a current of hydrogen.
4. Weiss and Neumann⁴⁴⁰. Reduction of the double fluorides with sodium in slight excess of equivalent quantities in a sealed iron cylinder at $1,000^\circ C$.
5. Wedekind and Lewis⁴³⁵, also Kuzel⁴⁰⁶. Heating the oxide with metallic calcium in an evacuated steel bomb.

REDUCTION OF POTASSIUM ZIRCONIUM FLUORIDE WITH SODIUM.

The first method tried for preparing amorphous zirconium was the reduction of the double fluorides with sodium as suggested by Weiss and Neumann, after the original method of Berzelius. The K_2ZrF_6 was finely pulverized and mixed with a slight excess of sodium, cut into small pieces. The whole charge was placed in an iron tube and the tube evacuated. It was then heated to $1,000^\circ C$. for 15 to 20 minutes. When the tube was cooled the zirconium had been reduced and the mass was a black porous material with white potassium fluoride through it. The mass was broken up and extracted with water and the excess of salts dissolved. A black powder was obtained which seemed to be contaminated with zirconium hydroxide. On digestion with 1:1 HCl the powder became more uniformly black, and was collected and carefully dried.

Analysis of this material showed no considerable purity of amorphous zirconium. On ignition 0.1400 gram increased in weight only 0.0004 gram, although on ignition the material changed from the black powder to the white oxide with incandescence. This increase in weight does not indicate very high-grade material, but subsequent observations indicate that probably the analysis was not fair, as precautions were not taken to purify the amorphous metal; these precautions include freeing the amorphous material from moisture and absorbed gases, which requires, according to Wedekind, that the material be heated to at least $1,000^\circ C$. in a high vacuum. The results of reductions made in this way were unsatisfactory, chiefly because this means afforded no suitable method of preparing anything like pure amorphous zirconium. By the reduction with sodium, impurities of iron and silicon were introduced in considerable

quantities, and many reductions were incomplete, perhaps through failure to evacuate the tube enough or from leaks in the joints permitting subsequent formation of ZrO_2 . Another important feature which became evident as soon as attempts were made to analyze the amorphous material was the great absorbent property of this form of zirconium. On igniting amorphous material, without first drying it and then freeing it of absorbed gases, the material frequently was found to have lost weight, even after having completely burned to the pure white oxide with every evidence (glowing, etc.) of oxidation.

The greatest difficulty experienced with this method was in washing the soluble salts from the amorphous metal. If amorphous zirconium is allowed to stand in pure water, flocculent zirconium hydroxide separates in the solution, and is difficult to dissolve from the amorphous metal by treatment with hydrochloric acid. It is believed that much of the difficulty in getting pure metal by this means is largely in washing out the soluble salts and in the formation of the hydroxide during the process. Some samples of amorphous metal prepared in this way were gray instead of black because of much contamination with the white oxide.

Attempts to fuse this amorphous material resulted in failure, even when the material was heated as high as $2,000^\circ \text{C.}$, the melting point of aluminum-oxide crucibles. For some time the failure to sinter the amorphous metal at this high temperature led to the belief that the melting point of zirconium was much higher than $2,000^\circ \text{C.}$, but further investigation showed that the presence of oxides formed when the amorphous material was heated without first removing the occluded gases was responsible for the difficulty. According to the Bureau of Standards⁷ the melting points of certain metals are raised considerably by the presence of small quantities of oxides. Ruff and Martin⁸ have found that the melting point of vanadium is raised by the presence of oxides. If chromium is melted in a slightly oxidizing atmosphere or in impure hydrogen the apparent melting point obtained is above that of platinum, whereas the melting point of chromium is given as $1,520^\circ \text{C.}$ Later experiments have justified the belief that this influence of the oxides is true for zirconium. The manner of preparation, the subsequent treatment, and the poor grade of amorphous material obtained caused the sodium reduction of the fluorides to be abandoned for the better methods discussed below.

Weiss and Neumann, using the sodium reduction of purified K_2ZrF_6 , claim to have obtained in their best trials 97 to 98 per cent amorphous zirconium. A sample of their data is given below.

⁷ Burgess, G. K. and Waltenberg, R. G., Melting points of the refractory elements: I, Elements of atomic weights from 48 to 59: Bureau of Standards Scientific Paper 205, 1913, 90 pp.

⁸ Ruff, Otto, and Martin, Walter, Ueber reines Vandin: Ztschr. angew. Chem. Jahrg. 25, 1912, p. 49.

TABLE 22.—*Analysis of amorphous zirconium prepared by Weiss and Neumann.*

	I.	II.
Weight of Zr metal.....	0.0793	0.1006
ZrO ₂ found.....	.1048	.1333
Purity of metal.....per cent..	97.77	98.03

There seems to be some question about the calculations of Weiss and Neumann. The ratio $\frac{\text{ZrO}_2}{\text{Zr}}$ or $\frac{122.5}{90.6}=1.353$, therefore 0.0793 gram Zr should yield 0.1073 gram oxide; or there should be an increase in weight in the first case of $0.1073-0.0793=0.0280$ gram, whence the actual increase of weight was $0.1048-0.0793=0.0255$. The percentage of free zirconium oxidized then $\frac{0.0255}{0.0280} \times 100 = 91$ per cent free amorphous zirconium. In the second case, Weiss and Neumann had 91.8 per cent free zirconium.

The values calculated by Weiss and Neumann represent approximately the total zirconium in the sample and not the percentage of free amorphous metal. Samples of amorphous zirconium carefully prepared by the method of Weiss and Neumann and then heated in a vacuum for 2 hours at 200 to 300° C. gave the following analyses:

TABLE 23.—*Analyses of amorphous zirconium.*

	I.	II.	III.	
Weight Zr metal.....	0.2055	0.1000	0.2000	
Weight ZrO ₂ found.....	.2700	.1335	.2660	
Per cent free Zr.....	89.0	94.9	93.5	Average.
Per cent total Zr.....	97.0	98.6	98.3	98.0

These two analyses, made on separate samples, show some variance but compare favorably with the values of Weiss and Neumann. By this method Wedekind has prepared amorphous zirconium metal, which showed on analysis 93 per cent amorphous zirconium.

REDUCTION OF POTASSIUM ZIRCONIUM FLUORIDE WITH ALUMINUM.

Weiss and Neumann, whose work and suggestions have proved highly valuable aids in the present investigation, reduced potassium fluozirconate with the calculated amount of aluminum, thereby forming fairly pure amorphous metal. This method is largely utilized in the preparation of the so-called crystalline Zr by using a large excess of Al. Experiments were made using the theoretical amount of Al needed for the reduction of the K₂ZrF₆, according to the equation:



The experiments when made in a manner similar to the sodium reduction proved somewhat unsatisfactory, even though the reduc-

tion itself was complete, because the subsequent treatment and washing of the amorphous Zr free from soluble salts introduced impurities, due to the hydrolysis of the amorphous Zr. Subsequent drying and heating in vacuo gave a product of amorphous Zr which was only a little better than that obtained by the sodium reduction.

An intimate mixture of the K_2ZrF_6 and powdered Al was placed in a boat within an evacuated iron cylinder and heated externally by means of a blast lamp to $1,000^\circ C$. This temperature was maintained for from 15 to 20 minutes, although a sudden rise in the pyrometer reading at 600° to $700^\circ C$. indicated that the reduction temperature was much lower than $1,000^\circ C$., and that before reaching $1,000^\circ C$. the reaction had been complete. By this means a fairly high-grade product was obtained, but by subsequent washing with H_2O , dilute HCl, alcohol, etc., its purity was much reduced, the product containing not more than 85 to 90 per cent.

Indeed, the reduction was considered to be very good, but subsequent treatment failed to get the amorphous product free from impurities, so that the wet method of purifying amorphous Zr was abandoned for a method by which the excess salts were volatilized completely in the vacuum furnace.

REDUCTION OF POTASSIUM ZIRCONIUM FLUORIDE WITH ALUMINUM IN AN ARSEM VACUUM FURNACE.

Reduction of the fluorides with Al was tried in the Arsem vacuum furnace. It was hoped to make the reduction, which takes place at about $600^\circ C$. in the Arsem furnace, and by raising the temperature distill off the Al_2F_6 and KF in the vacuum of 1 or 2 mm. of mercury, leaving behind the amorphous Zr; then by raising the temperature still higher eventually to fuse the metal. A description of this furnace, with photographs of the equipment used, is given on page 115.

The charge was made according to the same reaction, $3K_2ZrF_6 + 4Al = 3Zr + 6KF + 2Al_2F_6$, or, theoretically, 7.85 grams K_2ZrF_6 to 1 gram Al.

As at first the presence of aluminum in some excess was deemed preferable, the charge was made up with 10 grams K_2ZrF_6 to 1.5 grams Al. The finely powdered and thoroughly mixed charge was placed in an alundum crucible and the temperature gradually raised to $600^\circ C$. After the reaction was observed to be over, the temperature was raised, the final temperature varying from $1,500^\circ$ to $1,600^\circ C$. In all the experiments tried, using a vacuum furnace, the results were practically the same. A fairly pure, black, and amorphous Zr metal was obtained.

Wedekind claims that when he reduces ZrO_2 with calcium metal and gets amorphous zirconium, this material sinters together at

1,000° C. On the basis that this is true, the amorphous zirconium should sinter at 1,000° C. in the vacuum furnace, but numerous attempts to sinter at this temperature met no success. In view of the fact that the melting point of pure zirconium is above 1,700° C., it is difficult to see how even partly sintered metal could be obtained at 1,000° C. unless the product contained low melting-point impurities, such as metallic calcium. At 1,500° C. this method has yielded a thimble-like porous mass that appeared to be partly coherent metal—that is, it retained its shape but broke down under a slight pressure. This material could be polished to give a bright metallic surface. Analysis of the first products when an excess of aluminum was used showed about 10 per cent of aluminum. On burning to the oxide, 0.2763 gram of the metal yielded 0.3902 gram. This weight of amorphous zirconium should yield 0.3738 gram of oxide. The excess weight of oxide is due to the formation of aluminum oxide. Thus the experiments showed that the temperature must be above 1,500° C. and the heating continued in the furnace to remove all of the excess aluminum.

Later trials, the mixture of K_2ZrF_6 and aluminum being heated to 1,750° to 2,000° C., yielded amorphous zirconium free from aluminum but contaminated with small amounts of oxide.

Attempts to sinter these samples in an atmosphere of evacuated air to white uniform metal with the appearance of iron or steel were without success at any temperature up to 2,000° C.

Analyses of the products showed that Al and K had all been volatilized by this treatment at high enough temperature. Oxide formation, however, was evident and was attributed to the oxygen remaining in the furnace after evacuation even to 1 to 2 mm. pressure.

Analyses of the metal thus obtained showed about 90 to 95 per cent zirconium. For example, 0.3790 gram of Zr prepared in the above manner yielded 0.4705 gram of oxide on ignition, which corresponds to 91.8 per cent of zirconium. Presence of the oxide undoubtedly accounts for the zirconium metal not running together, a superficial layer of oxide coating the particles of amorphous metal and preventing coalescence. It is well known that finely divided zinc or aluminum if contaminated with oxide will not run together even though heated far above the melting point. It is possible that these samples were contaminated with a little carbide, although analyses were made for carbides and no weighable quantities were found.

Not much variation in the result was obtained by using a deficiency or a large excess of the aluminum. By using an excess it was hoped to form the Al-Zr alloy, which would sinter down, the excess of aluminum finally volatilizing off. This did not happen with finely

divided aluminum because the excess Al was volatilized before the alloy formed, and sometimes some of the Al formed an oxide with the small amount of oxygen present, contaminating the Zr metal. A deficiency of Al seemed to yield more promising results, inasmuch as one or two trials yielded a few small semiporous metal beads mixed with the amorphous metal, which, however, were too small for identification as pure metal and too contaminated with oxide for accurate analysis.

The result of these trials in the Arsem furnace with the K_2ZrF_6 and Al proved that:

1. The reduction could be made in this manner.
2. The excess materials, Al_2F_6 and KF could all be volatilized.
3. That oxide formation prevented the sintering of the amorphous material into coherent metal.

The result of this reduction method when the oxide formation was overcome is given in the chapter on the preparation of the coherent metal.

REDUCTION OF ZIRCONIUM DIOXIDE WITH ALUMINUM.

In the first attempts to prepare coherent metal by aluminothermic reduction of the oxide the amorphous metal was obtained. When theoretical amounts of aluminum are mixed with ZrO_2 and the mixture heated gently, the reduction takes place slowly with a gentle glowing, but without enough evolution of heat to fuse any of the materials formed in the reaction. When the reaction is conducted away from the air amorphous zirconium remains mixed with aluminum oxide from which it can not be separated satisfactorily. As this method could not be made to yield pure amorphous zirconium it was abandoned.

REDUCTION OF POTASSIUM ZIRCONIUM FLUORIDE ALUMINO-THERMICALLY.

Reduction of K_2ZrF_6 aluminothermically was tried in an attempt to produce fused metal. The double fluorides are readily reduced when mixed with an excess of aluminum and the equivalent to the excess of BaO_2 or $KClO_3$. When the mass is ignited with a strip of magnesium ribbon the reaction takes place with considerable vigor. The temperature of the reaction, however, unless the mixture contains a large excess of aluminum and BaO_2 is not high enough to fuse the amorphous metal. The black amorphous material remains mixed with the other products and can not be easily separated.

REDUCTION OF POTASSIUM ZIRCONIUM FLUORIDE WITH MANGANESE ZINC LEAD AND SILVER.

Magnesium, zinc, lead, and silver were tried for the reduction of K_2ZrF_6 but for various reasons were found inferior to aluminum and were eventually discarded.

REDUCTION OF ZIRCONIUM DIOXIDE WITH MANGANESE AND ZINC.

Reduction of zirconia with magnesium or zinc yielded only a black mass containing much oxide of zirconium. Reduction with magnesium in an atmosphere of hydrogen yielded the hydride. These experiments were not carried further than to determine that the pure metal was not obtained.

PREPARATION OF AMORPHOUS ZIRCONIUM BY ELECTROLYSIS OF FUSED FLUORIDES.

Troost has said that crystalline zirconium can be prepared by the electrolysis of the fused potassium fluozirconate. This experiment was tried at two different times and each time the amorphous metal was obtained. The method used was as follows:

The fluorides, about 100 grams, were placed in an iron dish and heated in an electric muffle furnace until they fused. The anode was of carbon; in one trial the cathode was of copper, and in the other of carbon. The current used, from storage batteries, was one-half to 2 amperes at 6 volts. After electrolysis the fused mass was allowed to cool, when amorphous zirconium was found suspended through it. When the soluble salts were dissolved, a small amount of fairly pure amorphous zirconium was obtained in the form of the usual black powder. That amorphous metal is prepared by this reaction is in accord with the statements of some of the later authors.

COMMERCIAL METHOD FOR PREPARING AMORPHOUS ZIRCONIUM FROM CRUDE ORE.

Other methods for preparing amorphous Zr were devised, one of which in particular proved excellent for preparing cheaply a commercial grade of amorphous zirconium that would have as its chief impurity amorphous silicon, with iron, titanium, and possibly aluminum. This material may be obtained directly from the silicate ore, as follows:

Crude ore, oxide, zircon, or baddeleyite is fused with a small excess of sodium fluoride and later with cryolite, slightly more than the calculated amount of finely divided aluminum being added to reduce K_2ZrF_6 , Na_2SiF_6 , and Na_2TiF_6 , which are formed on fusion.

The fusion is made in a tightly closed iron crucible under a layer of salt to minimize the corrosive effects of the fluorides and prevent the amorphous metal formed from burning. Reduction is complete after clear fusion. The fused mass is allowed to cool while tightly covered. When cold, the mass is pulverized; the soluble salts extracted with water and dilute HCl, and the bulk of the amorphous silicon dissolved out with a concentrated solution of caustic soda. The amorphous zirconium is converted slowly into the hydroxide. To eliminate this hydroxide a subsequent digestion in 1:1 HCl is

required, and the material, which will sometimes run between 80 and 90 per cent amorphous zirconium, is then washed and dried in vacuo, the temperature gradually being raised to 200° C. At this temperature in a high vacuum most of the gases are removed.

REDUCTION OF THE SILICATE ORE WITH ALUMINUM AND FLUX OF SODIUM FLUORIDE.

A mixture of silicate ore (zirkite), sodium fluoride (moderate excess), and Al (theoretical amount) was fused in the Arsem furnace. The product was amorphous zirconium, but a very pure product under this manner of reduction was not expected. It was tried simply to see if the silicate ore was reducible under these conditions.

CHAPTER XIII.—PHYSICAL AND CHEMICAL PROPERTIES OF AMORPHOUS ZIRCONIUM.

With the purest samples of amorphous zirconium produced as described above, the following properties have been determined:

TABLE 24.—*Properties of amorphous zirconium.*

Physical Properties.

Atomic weight.—90.6 (from literature).

Alloys.—With one exception does not form alloys under ordinary conditions. Can be alloyed by heating with aluminum. Does not form amalgams.

Boiling point.—Very high.

Corrosion.—Remains unchanged at ordinary temperatures, but when suspended in water it seemingly reacts slowly to form the hydroxide.

Color.—Black; heated above $1,000^{\circ}$ C., gray metallic.

Electrical conductivity.—Very low; black amorphous nonconductor.

Fusibility.—According to Wedekind, it partly sinters at $1,000^{\circ}$ C., but author of this bulletin never observed fusion at such low temperature. Material apparently coalesces to form white coherent metal, looking like iron or steel, at a little above $1,600^{\circ}$ in a high vacuum in an atmosphere of exceedingly dry and pure hydrogen; if a small amount of air or oxygen is present, this fusion does not take place. Melting point is above $1,700^{\circ}$ C. When heated to $1,000^{\circ}$ C. the amorphous black metal changes to gray-colored material, taking a metallic polish.

Hardness.—Soft, velvety; ignited above $1,000^{\circ}$ C., granular.

Luster.—Metallic by polishing. Pressed into sticks under high pressure and polished material has the appearance of a solid gray metal.

Melting point.—Above $1,700^{\circ}$ C.

Occlusion of gases.—Absorbs or occludes gases readily; also seems to have much affinity for moisture.

Specific gravity.—About 4.0, but varies with the amount of heating. Amorphous metal heated in the high vacuum furnace gradually shrinks and specific gravity increases until coherent metal is obtained, which has a specific gravity of more than 6.0. Amorphous metal as ordinarily prepared has a specific gravity of about 4.0.

Volatility.—Does not volatilize at $2,000^{\circ}$ C. in vacuum of 1 to 2 mm.

Chemical Properties.

Combines readily with chlorine at low heat; in nitrogen it burns to nitride at a dull red heat. When heated in the air to a low red heat, it burns to ZrO_2 with a white incandescent glow. Is slowly soluble in 1:1 hot HCl. Dissolves readily in HF, even dilute. Is only slowly soluble in HNO_3 and somewhat more soluble in hot concentrated HCl. Dissolves in ordinary fusion agents such as $K_2(SO_4)_2$, Na, etc. Amorphous Zr formed by the reduction of K_2ZrF_6 with Na dissolves in water, forming bluish colloidal solutions that readily pass through filter paper.

The possible uses of the amorphous metal may be summed up as follows:

1. *In flashlights.*—If the amorphous metal is mixed with KNO_3 , $KClO_3$, or other oxidizing agent, it burns with a bright light. It is doubtful whether the amorphous metal would be cheap enough to use in place of the usual material.

2. It might be used as some of the other amorphous metals are used for lining molds in making castings, although the use of zirconium in the ferroalloy seems somewhat in question at the present.

CHAPTER XIV.—EXPERIMENTAL WORK ON THE PREPARATION OF COHERENT ZIRCONIUM.

METHODS OF PREPARATION.

The literature on the preparation of the fused metal is limited. Only a few authors have presented methods of obtaining this variety of zirconium. They are listed below:

1. Kuhne⁴⁰⁵ has suggested the reduction of the oxide of TiO_2 , V_2O_5 , ThO_2 , and ZrO_2 with Al and BaO_2 .

2. Weiss and Neumann⁴⁴⁰ suggested the reduction of the oxide by the alumino-thermic method, using KClO_3 for production of enough heat for the reaction. They admit the method does not give good results.

3. Weiss and Neumann⁴⁴⁰ have produced Zr by distilling the Al from the crystalline Al-Zr alloy in vacuo.

4. Kuzel and Wedekind⁴⁰⁶ have produced Zr by sintering amorphous Zr (from Ca reduction of the oxide) at $1,000^\circ \text{C}$.

5. Lely and Hamberger⁴⁰⁷ reduce the anhydrous chlorides or fluorides with Na in vacuo and claim to sinter the product.

6. Ehrich-Graetz-Podszus⁴⁰² ignite a pressed rod of finely ground material close to its melting point in an atmosphere of H_2 with some halide. The metal sinters.

7. Moissan⁴¹⁴ and also Troost⁴²³ have prepared coherent metal by reducing ZrO_2 with carbon in the arc furnace.

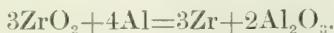
ALUMINO-THERMIC REDUCTION METHOD.

The alumino-thermic, otherwise known as the Goldschmidt process, was one of the first methods investigated for the production of coherent metal. This method, which is much recommended for producing carbon-free pure metals and metal alloys, is based on the reduction of metallic oxides with powdered aluminum. Aluminum has a greater affinity for oxygen than most other elements, and hence it is possible, under properly controlled conditions, to cause aluminum to extract the oxygen from practically all the other metallic oxides. This is because aluminum has a higher heat of formation than other metallic oxides, and reactions go in the direction in which the development of heat is highest.

In many cases, as with Al and Fe_2O_3 , the mixture of the oxide with the powdered aluminum is made in molecular proportions for proper reduction, with possibly a slight excess of aluminum, the reac-

tions, when once started by burning magnesium ribbon or an electric spark, being vigorous enough to supply all the heat necessary to reduce the oxide and to run the metal together in a button. To reduce other oxides more aluminum must be used, with corresponding additions of readily reducible oxides, such as BaO_2 or KClO_3 , in order to obtain the temperature necessary to fuse the metal. Still other metals when reduced have a specific gravity that is not enough greater than that of the slag material to permit good separation of a metallic button. This difficulty is overcome by adding fluxing materials that lighten the slag or render it more fluid.

There is not enough difference between the heats of formation of ZrO_2 and Al_2O_3 to give good results by the Goldschmidt reaction. Weiss and Neumann have found the heat of formation of ZrO_2 to be 1,958.7 calories per gram of zirconium, which gives for one molar weight of ZrO_2 formed a heat of formation of 177.5 calories. The reaction between ZrO_2 and Al is represented by the equation:



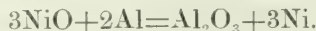
Heat of formation of $2\text{Al}_2\text{O}_3 = (131.2 \times 6) = 785$ calories

Heat of formation of $3\text{ZrO}_2 = (177.5 \times 3) = 532.5$ calories

A difference of ----- 253 calories, or,

For the formation of 1 molar weight Al_2O_3 126.5 calories

As compared with the reaction between nickelous oxide and Al:



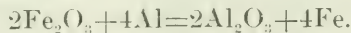
Heat of formation $\text{Al}_2\text{O}_3 = (131.2 \times 3) = 393.6$ calories

Heat of formation $3\text{NiO} = (61.5 \times 3) = 184.5$ calories

A difference, for 1 molar weight,

Al_2O_3 , of ----- 209.1 calories

Also compared with the reaction between ferric oxide and Al:



Heat of formation $2\text{Al}_2\text{O}_3 = (131.2 \times 6) = 787.2$ calories

Heat of formation $2\text{Fe}_2\text{O}_3 = (65.9 \times 6) = 395.4$ calories

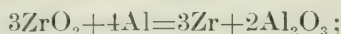
A difference of ----- 391.8 calories, or,

For 1 molar weight Al_2O_3 ----- 195.9 calories

A comparison of these reactions shows that:

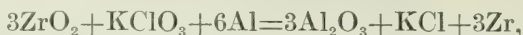
- (1) With Fe_2O_3 an excess of 98 calories per gram atom Al used;
 - (2) With NiO an excess of 104 calories per gram atom Al used;
 - (3) With ZrO_2 an excess of 63 calories per gram atom Al used;
- which is evidence that the amount of heat evolved during the reduc-

tion of ZrO_2 is relatively lower than in that of NiO or Fe_2O_3 . By experiment it was found that a mixture formed according to the equation:



that is, 271.8 grams ZrO_2 to 108 grams of powdered Al, gave a very slow reduction, only enough heat being generated to cause a dull-red glow, and yield a mixture of Al_2O_3 and amorphous zirconium. The ordinary means of starting the reaction was of no avail, because not enough heat was evolved to promote the reaction. A mixture prepared in the above proportions is, however, reduced if it is heated by external means in a blast furnace until the reduction is well started. Under some conditions this reduction yields a suboxide of zirconium that has a velvety black appearance and occasionally is mistaken for amorphous zirconium.

Experiments then were tried using varying quantities of aluminum and ZrO_2 with BaO_2 or KClO_3 . By the addition of enough KClO_3 to comply with the formula,



a mixture was obtained that reacted with considerable vigor. For laboratory trials the following quantities of material were used: 90 grams of ZrO_2 , 30 grams of KClO_3 , and 40 grams of Al.

Although the reaction with these quantities of materials evolved considerable heat, the yield of beads of metal was poor, because of the small quantity of material used, and because the specific gravity of the zirconium metal was almost the same as that of the slags formed in the reaction, so that the metal would not separate.

In these experiments the mode of procedure was to grind finely and to mix intimately the constituent materials, then place them in a magnesite-lined fire-clay crucible and embedded in Sil-o-cel. A piece of magnesium ribbon was placed in the mixture so that it could be easily lighted. When the magnesium ribbon burned down, it ignited the mixture, and then a fire-clay brick was dropped over the mouth of the crucible to retain the contents. The reaction was short but very violent, and an intense heat was evolved. The material was allowed to cool and then was broken away from the crucible.

The zirconium metal was in the form of small beads and finely divided metal disseminated throughout the slag. An appreciable amount of amorphous, unfused zirconium was also found. The metal thus prepared was too brittle and friable to permit its entire recovery from the slag; the beads only, in most trials, could be obtained free from slag. Many of these beads were coated with a thin film of gray-white oxide or yellow nitride formation. The slag material from this reduction was afterwards mixed with more

aluminum and fused in the Arsem furnace. The metal regulus obtained, which was more or less porous, separated from the overlying slag material. Possibly in producing zirconium metal, if the heat of fusion were maintained longer the yield of metal would be materially increased.

Several samples of beads prepared at first yielded appreciable amounts of iron, titanium, and silicon on analysis. Investigation showed that these impurities, with the exception of the titanium, were all contained in the materials used in the reduction. On purification of all these materials samples of metal were prepared which gave the analysis following—the impurities of iron and silica being in the aluminum.

TABLE 25.—*Analyses of zirconium metal obtained by aluminothermic reduction of ZrO_2 .*

[Samples carefully cleaned of all surface coatings.]

<i>Analysis No. 1:</i>	Per cent.
Fe, Al-----	1.2
Ti-----	.2
Si-----	.4
Zr-----	98.1

99.9

Analysis No. 2.—(After the aluminum had been put through a Wetherill magnetic separator much better results were obtained.)

	Per cent.
Fe-----	0.12
Ti-----	.4
Si-----	.4
Al-----	trace
Zr-----	99.0

99.92

Analysis No. 3.—(Using another sample of Al that contained less impurity.)

	Per cent.
Fe-----	0.02
Ti-----	.40
Si and Al-----	.08
Zr-----	99.50

100.00

Another analyst found this material to contain:

	Per cent.
Zr-----	99.40
Ti-----	.45
Fe-----	.01
Al and Si by difference-----	.14

100.00

It is of interest to note that samples of ground aluminum metal marked "c. p." contained 1 per cent of iron that could be removed

by the Wetherill magnetic separator. The iron was in small pieces that were probably introduced in grinding. It was soon found that the purity of the beads of metal obtained by the alumino-thermic method depended entirely on the purity of the materials used in the reaction. Attempts to improve the yield of beads in the formation of a metal regulus free from slag were more or less unsuccessful. Further experiments along this line were dropped because: (1) the yield of metal was very poor; (2) it was impossible to obtain 100 per cent Zr metal without entire purification of the several constituents. The aluminum would have to be prepared from purified aluminum salts.

If the yield could be increased the method might be used for obtaining the metal and its alloys on a commercial scale.

PREPARATION OF COHERENT METAL IN ARSEM FURNACE.

Weiss and Neumann, as well as earlier investigators, have suggested that aluminum can be distilled from some of its alloys in a high vacuum furnace, a pure metal being left; and on this basis they attempted to prepare pure zirconium metal in the coherent form by heating the zirconium-aluminum alloy in the electric arc. If it is true that aluminum may be distilled from zirconium metal by passing the electric arc between two sticks of the alloy, it must also be true that aluminum may be distilled in any vacuum furnace from the alloy, providing the vacuum and temperature are high enough. Some of the experiments which are listed below have been based upon this same idea and will be described later. The Arsem vacuum furnace, as has been stated, was first used in attempts to prepare amorphous zirconium from the potassium fluozirconate mixed with aluminum powder. This furnace and its equipment are described on pages 115 to 116.

As with the amorphous metal, as there was no attempt to reach temperatures above $2,000^{\circ}$ C., aluminum oxide crucibles and later ordinary alundum crucibles were used. The furnace could easily be heated to $2,000^{\circ}$ C. in 20 minutes under a vacuum of 1 millimeter, but the heat obtained within the furnace seemed to vary considerably with the vacuum, so that only approximate determination of temperature could be made by observation of the current consumed. Some difficulty is experienced with this type of furnace in using the optical pyrometer, because a small amount of arcing in the interstices of the helix vitiates somewhat the readings of this instrument. The vacuum was supplied by a rotary oil pump that would give 1 millimeter vacuum in the entire apparatus in a very few minutes.

In the first trials in the Arsem furnace potassium fluozirconate and aluminum were heated to about $1,400$ or $1,500^{\circ}$ C. Amorphous zirconium was obtained, mixed with some of the salt and oxide that

remained in the crucible. These experiments have been described in the chapter on amorphous zirconium.

In trials to prepare amorphous zirconium, using only 80 per cent of the calculated amount of aluminum with the potassium fluozirconate, a number of small thimbles of zirconium were obtained free from aluminum; they were porous, but were rigid enough to hold their shape under some pressure. This material was concluded to be partly sintered metal, because when polished on the surface it gave the gray-white appearance of coherent zirconium metal, but it contained some oxide, and the only conclusions that could be drawn were that either the cast-iron container of the furnace leaked and allowed moisture, which reacted with the metal, to get into the furnace or that the oxygen from the small amount of air in the container combined with the zirconium, forming some oxide, or that some carbide was formed.

As has been stated, the Bureau of Standards has found by experiment that a small amount of oxide in a metal decidedly raises the melting point. With chromium, about 2 per cent of oxide raised the melting point some 200° C. It was, therefore, concluded that the reason why the amorphous zirconium did not sinter properly was because oxygen combined with the metal, forming some oxide that coated the particles of amorphous zirconium and prevented them from coalescing. As the melting point of zirconium oxide is nearly $3,000^{\circ}$ C., a small amount of oxide could well account for this; and as the specific gravity of the oxide and the sintered metal are not far apart, this material was probably a physical mixture of the two. The obvious remedy of such difficulties would be to exclude any oxygen or air from the reaction.

An attempt was made to remove all of the oxygen or air from the apparatus by using an excess of aluminum. Potassium fluorzirconate was mixed with twice the necessary quantity of aluminum and the temperature raised to nearly $2,000^{\circ}$ C. in the hope that the excess of aluminum would take up all the oxygen from the air in the furnace and form aluminum oxide that would not remain mixed with the metal. But the aluminum distilled so readily in the high vacuum of this furnace that the difficulty was solved in part. Observation of the changes that took place in the furnace showed that the thimble of amorphous zirconium was formed, as previously described, and that on continued heating this thimble gradually shrunk until a small button of metal was left. When this button was cooled and taken out of the furnace, it was coated with a layer of either carbide or suboxide and some oxide. The metal when broken and polished showed the white color of the sintered metal, but was still porous. It was, however, very hard, scratching glass with ease, and much like the sintered metal obtained by aluminothermic reduction; it

was insoluble in all acids except boiling aqua regia and hydrofluoric acid, and when the outside layer of oxide, etc., was dissolved with dilute hydrofluoric acid a fair grade of white, brittle metal was obtained. Thus the experiment had accomplished what had been considered impossible, namely, the fusion of the amorphous metal.

Analysis of this metal that had been heated to $1,900^{\circ}$ C. gave the following results:

Analysis of fused metal.

Fe, Ti, Si	0.5
ZrO ₂ (ZrO)	4.0
Zr	95.0
	99.5

The results of these experiments led to the conclusion that if the presence of oxygen in the furnace could be prevented, perhaps a fairly good coherent metal could be obtained.

EXPERIMENTS IN THE ARSEM FURNACE WITH AN EVACUATED ATMOSPHERE OF HYDROGEN.

The next experiments tried with this mixture were in an atmosphere of hydrogen, great precautions being taken that the hydrogen should be previously dried and free from contamination. The hydrogen was prepared by means of the Kipp generator, using zinc and dilute sulphuric acid. To remove any traces of oxygen, the hydrogen was first passed through a solution of chromous chloride prepared by the action of hydrochloric acid and zinc on potassium dichromate and having the clear blue color of a properly prepared solution. The preparation of this solution is described by Roscoe and Schorlemmer¹⁰³. After the hydrogen passed through the chromous chloride solution it passed through neutral silver nitrate solution that contained silver sulphate in suspension; then through potassium hydroxide solution and successively through U tubes containing soda lime, fused calcium chloride, and phosphorus pentoxide. Then the hydrogen was passed directly into the furnace and through it for at least two hours before any runs were attempted, but the results showed that more than two hours were necessary to remove all traces of air.

When the potassium fluozirconate was heated with an excess of aluminum under these conditions, no great difficulty was had in causing the amorphous zirconium, which formed first, to run down into a button of more or less coherent metal, although the product was still somewhat porous. In fact the amorphous material which forms at first seems to have a definite melting point somewhat above $1,700^{\circ}$ C. Whether an excess, a deficiency, or the theoretical amount of aluminum was used, the melting point was the same. This definite

melting point indicated that the material was pure. It may be that in this material which seemed to run down to the bottom of the crucible and melt was some aluminum that lowered the melting point, but it is believed that the melting point of amorphous zirconium should be in the neighborhood of $1,700^{\circ}$ C. The product contained no oxide, so far as could be determined, nor any carbide that might have come from the carbon vapors from the heated helix or from the small amount of arcing that occasionally took place when the helix became old. The hydrogen was allowed to pass through the apparatus all the time; and it is believed that any carbon, methane, or ethylene vapors that formed were largely removed by the hydrogen. It is believed that when the hydrogen is very pure and dry very little carbide forms in the metal, as has been suggested by Ruff.^h The only contamination of the zirconium metal thus formed seemed to be from the iron and silicon of the aluminum used in the reduction.

Analyses of metal prepared in this way are given below:

Analyses of metal prepared in an atmosphere of hydrogen, 1 mm. pressure.

Analysis No. 1.— K_2ZrF_6 with twice theoretic weight aluminum:

Fe, Al, Ti	1.7
ZrO ₂ , Si	0.3
Zr metal	98.9
	100.0

(A very little carbide was found in this sample.)

Analysis No. 2.— K_2ZrF_6 with 80 per cent theoretical weight aluminum. Al passed over magnetic separator to remove free iron:

Fe, Si	0.2
Al	Absent.
Zr	99.5
	99.7

When the hydrogen used in the furnace was moist and impure, the white MgO crucibles became black on heating to a high temperature and some aluminum carbide formed on their surface, but when the hydrogen was very dry and pure and the helix had been previously heated, the crucibles remained white. To prevent any solid carbon or other materials from falling into the melt an alundum tube was ground down to fit into the top of the crucible and cut off at the proper length to extend above the top of the helix. Although some of the salts condensed at the top of the tube, the arrangement effectually prevented solid carbon from coming directly in contact with the contents of the crucible.

^h Ruff, Otto, Ueber Carbides: Ztschr. Electrochem, Bd. 24, 1918, p. 157.

The analyses given above are the average of analyses of two different chemists and shows the result obtained when precautions were taken to avoid all traces of moisture, which seems to catalyze the formation of carbides, and to prevent solid particles from the helix from falling into the crucible.

This sample was prepared by treating the metal with dilute hydrofluoric acid to dissolve any coatings of oxide or carbide. The metal had a gray-white appearance like gray iron. Because of the impurities in the aluminum a higher grade of zirconium could not be prepared by this method.

Powdered aluminum purchased on the market was analyzed. The first sample, which was marked chemically pure and was very finely powdered, gave the following analysis:

Analysis of "chemically pure" powdered aluminum.

Aluminum-----	99.1
Iron-----	.33
Silicon-----	A considerable amount, not determined.

This sample of aluminum contained oil, which, although it was volatile and could be distilled away, nevertheless contaminated the aluminum considerably. With this aluminum not much better than 98 to 99 per cent zirconium could be prepared by the method described above because all of the iron and silicon in the aluminum remained with the zirconium. Other samples of aluminum analyzed ran about the same in iron and silicon, and with these samples of aluminum, with one exception, it was impossible to get much better than 99 per cent zirconium. It was thought, however, that if the aluminum were pure perhaps a very high grade of zirconium could be made.

TABLE 26.—*Analysis of other samples of aluminum.*

A.		B.	
Si-----	0.03	Si-----	0.07
Fe-----	0.57	Fe-----	0.19
Al-----	99.1	Al-----	99.50
C.		D.	
Si-----	0.13	Si-----	0.10
Fe-----	1.43	Fe-----	2.0
Al-----	98.5	Al-----	97.8

Samples (A) and (B) were marked chemically pure.

In regard to the purity of the zirconium, it is doubtful whether Weiss and Neumann, by their method of distilling the aluminum from the zirconium-aluminum alloy, prepared zirconium more than 99.5 per cent pure, as they make no mention of having purified their aluminum metal.

On looking over the various methods that might be used for the preparation of pure aluminum, it was found that Mallett had prepared some pure metal as a gray powder by the action of sodium on the bromides of aluminum, but examination of the sodium in stock showed that it still contained some iron and silicon; therefore this method could not be used with the materials at hand. Production of aluminum by the electrolysis of pure white salts would have proved tedious and therefore this was also abandoned. As it had been found that aluminum distills easily in the Arsem furnace, experiments were started to see whether a pure aluminum metal could not be distilled free from iron and silicon. The first trials were made using a fused quartz tube, but the aluminum reduced the quartz (silicon dioxide) to amorphous silicon, so that the experiments with this tube were a failure.

After some difficulty an alundum tube 1 inch in diameter and 12 inches long was obtained. This was sealed at the bottom into an alundum crucible with some pure aluminum oxide paste and distillation of the aluminum was attempted in it.

The aluminum, condensed in small round or oval drops about one-eighth inch in diameter, on the inside of the tube just above the heating part of the helix. These pieces of white Al metal clung tenaciously to the tube, but after being scraped off and cleaned from adhering alundum showed practically no iron or silicon on analysis.

EXPERIMENTS TO REDUCE POTASSIUM ZIRCONIUM FLUORIDE WITH OTHER METALS THAN ALUMINUM IN THE ARSEM FURNACE.

Owing to the difficulty in obtaining Al of sufficient purity, trials were made of other metals that analysis showed to be free of iron and silicon. Silver was tried, but the removal of any excess of silver alloyed with the zirconium proved very difficult, and the silver did not reduce the zirconium from the fluorides satisfactorily. Lead, sodium, zinc, and magnesium were also tried, but all of them were too volatile for use in the high vacuum of the Arsem furnace and distilled away without reducing the zirconium. It was hoped that nearly pure magnesium could be used in hydrogen at ordinary pressures to make the reduction and that the salts in the fused mass could be volatilized in the Arsem furnace, but again difficulty was experienced because the magnesium was so volatile and only partly reduced the zirconium. In the presence of hydrogen and magnesium the zirconium formed a hydride. The use of these metals for the reduction in this furnace was abandoned because they showed no advantage over aluminum.

DISTILLATION OF ALUMINUM FROM ZIRCONIUM-ALUMINUM ALLOY IN THE ARSEM FURNACE.

As has been stated, Weiss and Neumann claim to have distilled the aluminum from the so-called crystalline (alloy) zirconium, Zr_3Al_4 , leaving pure fused metal. This distillation was attempted in the Arsem furnace. The boiling point of aluminum at atmospheric pressure is near $2,000^{\circ} C.$, but under the high vacuum of the Arsem furnace this metal should distill at not over $1,200^{\circ} C.$, and the removal of aluminum from an alloy should not be difficult at the high temperature attainable.

The preparation of this crystalline alloy is described in the chapter on zirconium alloys. On the first trials the alloy was placed in the crucible in small pieces having a cross section of about 1 mm. When the temperature was raised, but before fusion was noted, a reaction similar to the deflagration of salts was observed; it was so violent that much of the aluminide was blown out of the crucible and lost. After continued heating, however, the material that remained in the crucible fused. Analysis showed that all of the aluminum had not been removed. On later trials, when the heating was prolonged a much purer product was obtained. By pressing the Zr-Al alloy into small sticks and heating as before, a metal regulus was prepared which contained some aluminum. To remove the last traces of aluminum from the alloy proved difficult. The metal obtained was hard and brittle and similar in every respect to that previously prepared by other methods.

EXPERIMENTS WITH THE ARC VACUUM FURNACE.

An arc vacuum-furnace was prepared especially for this work, in order that, if necessary, the aluminum might be distilled away from the zirconium in the absence of all carbon. This arc furnace (see Pl. II, p. 116) was made after a consideration of the work of Weiss and Neumann, but its design is more or less original with the authors. The furnace is water-cooled and has an observation window of mica at the top. The electrode holders, which are fastened in place by insulated stuffing boxes, are made of three-fourths-inch brass tubing that can be slipped up and down in the stuffing boxes. The pieces of zirconium-aluminum alloy to be arced are fastened into the electrode holders so that the arc passes between them. The furnace is built in two parts, the base being fitted to the body with rubber gaskets and fastened together with iron bolts. The inside diameter of the furnace is 12 inches and the height 10 inches.

At first some difficulty was experienced in pressing zirconium alloy into sticks, but some trials showed that this could be done by simply wetting the finely ground material and using a very high pressure in a screw press. Figure 2 (p. 116) shows the apparatus

used in these experiments. The mold consisted of four quarter sections of steel held in place by iron rings, the apparatus being made in quarter sections so that it could easily be taken apart to remove the pressed metal. Several plungers of hardened steel were used, their length depending on the amount of material to be pressed.

After pressing the sticks were placed in a combustion tube and heated in a current of hydrogen until they partly sintered and were hard enough to be used directly in the arc furnace. Some of the sticks received preliminary heating in the Arsem furnace. After the heating the sticks could be handled with little danger of breaking and were good conductors of electricity.

When the sticks of Zr_3Al_4 alloy were fastened into the electrode holders the furnace was closed, water was circulated through the jacket, and the entire apparatus was filled with dry, purified hydrogen. After the oxygen of the air had been completely displaced the apparatus was evacuated down to about 5 mm. pressure and the arc started, 40 to 60 volts being used. With 60 volts the process of fusing the metal and collecting the beads of metal that dropped from the electrodes was rapid. The beads were caught in an aluminum oxide crucible.

The first arcing removes most of the aluminum, leaving a product containing about 90 per cent zirconium; a second and a third arcing remove most of the remaining aluminum. One of the best products obtained in this way yielded about 99.6 per cent Zr metal.

Composition of zirconium fused in atmosphere of hydrogen.

Si	0.05
Fe	.10
Al	(?)
Zr	99.6

A small amount of zirconium suboxide or hydride was formed during the reaction, as evidenced by a superficial black coating on the metal beads.

This grade of metal does not at first seem to compare with the metal of Weiss and Neumann, but their method of analysis may be questioned. They used the method described by J. Thomas Davis²⁴⁸ in which the zirconium is precipitated from faintly hydrochloric acid solution by means of sodium iodate. The authors have always obtained low results when the precipitate obtained by sodium iodate is washed thoroughly with cold water. When the precipitate from a solution containing both Zr and Al is washed with sodium iodate solution and then with dilute ammonia, the ignited oxides give a weight equal to the sum of the weights of ZrO_2 and Al_2O_3 . Also, the amounts of iron and silicon that must have been in the

original aluminum used have not been determined in Weiss and Neumann's samples.

The white coherent metal obtained was very similar to the samples previously prepared. It had a hardness of about 5, would scratch glass, and was quite brittle. A thin piece of it could be broken in the fingers.

CARBON REDUCTION OF ZIRCONIUM OXIDE.

Attempts were made to reduce zirconium oxide with carefully prepared sugar charcoal. According to Greenwood⁴⁰³ and to Pringⁱ zirconium oxide is reduced with carbon at about 1,400° C. When the pure charcoal and pure ZrO_2 were intimately ground together and heated in theoretical proportion to 2,000° C. in the Arsem furnace, the resulting product proved to be a mixture of small particles of white zirconium metal contaminated with zirconium oxide and carbide. For satisfactory reduction the mixture must be very intimate. This method was not investigated further owing to the difficulty in getting a pure zirconium metal. Analyses are not given, but it is estimated from a rough determination that about 60 per cent of the ZrO_2 was reduced.

ⁱ Pring, J. N., The formation of some carbides: Trans. Chem. Soc. t. 93, 1908, p. 2101.

CHAPTER XV.—PHYSICAL AND CHEMICAL PROPERTIES OF COHERENT METAL.

The physical and chemical properties of coherent zirconium metal are tabulated below: they are essentially those that have been described for the sintered (reguline) metal by Wedekind and also by Weiss and Neumann. This metal has of course crystalline structure but should not be confused with the properties given later for the crystalline alloy. These properties have been determined on 39.5 per cent metal prepared as described in this bulletin. Small amounts of iron and silicon present in these samples may have affected some of the properties of the metal.

TABLE 27.—*Properties of coherent zirconium.*

Physical Properties.

Alloys.—Does not dissolve in lead, tin, or silver by simply heating above their respective melting points. Will alloy with silver, aluminum, and iron when heated above the melting point of zirconium in the Arsem furnace. Alloys of silver, iron, nickel, or aluminum are easily made by simultaneous reductions at high temperatures (Goldschmidt's process). Does not amalgamate.

Corrosion.—Does not rust or tarnish on long standing in the laboratory; when polished remains bright white, like polished nickel.

Color.—White, metallic.

Electrical conductivity.—Fairly good conductor; not as good as iron.

Fusibility.—Can be readily sintered under proper conditions away from the air at about 1,600° C.

Hardness.—About 4 to 5 on the Mohs' scale, according to method of preparation and purity of samples. Pure samples were less hard than the more impure metal. All samples of the metal readily scratched glass. As would be expected, the metal is quite brittle and can easily be broken by lightly pounding with a small hammer. At a red heat the metal is still very hard but less brittle. The hardness on the Shore scleroscope is 40 to 45.

Luster.—White, metallic; takes a fine polish like nickel.

Melting point.—Above 1,700° C. The Bureau of Standards found the melting point of the metal, as prepared by various authors, from 1,400° C. to 2,200° C. In recent trials the metal prepared by the author of this bulletin appears to melt at very close to 1,700° C. in a rarified atmosphere of pure dry hydrogen.

Occlusion of gases.—When samples of zirconium are fused in pure dry hydrogen and rapidly cooled, it exhibits an effect similar to the so-called "spitting" of silver. When silver is fused it dissolves oxygen and on cooling the oxygen is evolved, causing the "spitting" and leaving the metallic mass porous. Zirconium similarly treated in hydrogen shows

the same porous appearance. This porosity is not observed in samples prepared by the Goldschmidt process.

Specific gravity.—Partly sintered amorphous zirconium has a specific gravity of 4.39. The specific gravity of the alumino-thermic 99.5 per cent zirconium is 5.55, and that of 99.5 per cent coherent metal prepared by the reduction of K_2ZrF_6 with aluminum was 6.06. The specific gravity of zirconium, as of other metals, varies with the method of treatment.

Chemical Properties.

The white metal is much less chemically active than is the amorphous metal and does not readily react with chemical reagents at ordinary temperatures. In a solid piece it can be heated to a bright red in the blast flame with no more than a very thin bluish superficial oxidation, and when finely divided can be burned in the air by heating to a white heat. The white metal is insoluble in all acids except aqua regia and hydrofluoric acid; it dissolves easily in hydrofluoric acid (1:1), but to dissolve 1 gram of the solid metal by digesting in an excess of aqua regia requires at least five hours. The metal is not readily dissolved by fusion with bisulphates, caustic soda, etc.

Some suggested uses for coherent white zirconium metal are as follows:

1. As a substitute for platinum in certain cases on account of its acid-resisting properties. It can not, however, be used in connection with hydrofluoric acid.
2. For electrodes. When the alumino-thermic metal was used as the anode in a sulphuric acid solution, the metal went into solution, dissolving off the anode but not depositing on the cathode.
3. In the manufacture of rust-resisting apparatus. The alloys would be preferable for such a purpose.

CHAPTER XVI.—OBSERVATIONS ON THE PREPARATION OF ZIRCONIUM ALLOYS.

CRYSTALLINE ZIRCONIUM ALLOY.

According to Weiss and Neumann, the metal described in the literature as crystalline zirconium is an aluminum-zirconium alloy containing about 72 per cent zirconium and 27 per cent, or more, aluminum. Some analyses yield more than 27 per cent aluminum, but nevertheless indicate that the so-called crystalline zirconium is merely a zirconium-aluminum alloy.

The method of preparing this alloy, as suggested by Weiss and Neumann and others, is to place the potassium fluozirconate in a carbon dish and fuse in a furnace. When the fusion is complete, at about 900° C., one and one-half times as much by weight, of aluminum as fluozirconate is added a little at a time, and the fused mixture heated about 15 or 20 minutes. During this fusion a vigorous reaction takes place. When the reaction mixture is quiet the whole mass is covered with a mixture of potassium and sodium chlorides and allowed to cool. If the reaction has been done properly, the zirconium-aluminum alloy collects in a button in the bottom of the dish and the fused salts remain as a perfectly white mass on top. The button of aluminum alloy breaks away cleanly from the fused mass, and flat, platelike crystals, which are apparently monoclinic, are to be seen on its surface. If the alloy is broken up and treated with a strong solution of caustic soda until all of the excess aluminum is dissolved and the mass is then treated with 1:1 hydrochloric acid to remove any hydroxides of zirconium that are formed, the silver-white crystals of the so-called crystalline zirconium can be filtered off and dried. They are very insoluble in acids, are hard enough to scratch glass and do not oxidize on heating in a flame at a bright red heat. Perhaps the exceeding inertness of this compound has caused it to be confused with zirconium metal. If all of the excess aluminum could be removed from the mixture of crystals, the compound would undoubtedly be represented by the formula Zr_3Al_4 , and it is evidently a definite crystalline chemical compound of zirconium and aluminum.

TABLE 28.—*Analyses of zirconium alloys.*

An analysis of one of these alloys gave:	Per cent.
Al -----	30
Zr -----	68
Fe -----	1
Ti -----	Very little.

A second analysis of a purer product was as follows:		Per cent.
Zr	-----	70
Fe	-----	.03
Si	-----	.05
Al	-----	29.9
Ti	-----	Not enough to determine.
		99.98

This alloy when made directly from zirkite ore shows much silica:

Zr	-----	74.47
Si	-----	11.35
Fe	-----	.84
Al	-----	13.10
Ti	-----	Not determined.
		99.76

Zirconium aluminide seems to be the commonest alloy of zirconium that has been prepared in the chemical laboratory. It can easily be prepared directly from zirkite by fusing the latter with sodium fluoride and then adding the aluminum. Prepared in this way the alloy is more crystalline and the crystals appear larger, but they contain the silicon from the silicate ore. Possibly this alloy when made with a small amount of aluminum so that this metal is not in excess might have commercial use. The alloy can be prepared also from zirconium oxide by fusing with sodium fluoride and then adding the aluminum. If aluminum is not in excess, amorphous zirconium is formed and the aluminum does not separate in a clean condition from the mass. The crystalline alloy has also been made aluminothermically by using a large excess of aluminum.

ZIRCONIUM-SILVER ALLOY—LEAD AND TIN ALLOYS—AMALGAMS.

If metallic silver is added to the aluminothermic reduction described under the preparation of zirconium metal, a zirconium-silver alloy may be made. As prepared in the laboratory this zirconium-silver alloy contained between 10 and 20 per cent silver and by treatment with acids yielded finely divided cubical crystals that had a beautiful appearance under the microscope. Attempts to prepare a lead alloy or a tin alloy were failures, as were attempts to melt the coherent metal mixed with silver or lead or tin. For example, some pieces of the coherent metal were placed in a fire-clay crucible and covered with lead, and in another instance with tin, and heated considerably above the melting point of the lead or tin, but the coherent zirconium did not seem to dissolve in these metals and, therefore, no alloy could be formed. Attempts to form amalgams with either amorphous or coherent metal were failures.

FERRO ALLOYS.

By alumino-thermic reduction, four samples of ferrozirconium were made which analyzed, respectively, 30, 70, 73.5, and 81.9 per cent zirconium. In this alumino-thermic reduction, however, no satisfactory separation of ferrozirconium was obtained when the zirconium content of the alloy was high. Grenagle has stated that ferroalloys containing 60 to 90 per cent zirconium can be prepared that are malleable and ductile, but none of the alloys prepared by the author were; several of them, however, were hard enough to scratch glass and were brittle, their brittleness increasing with the proportion of zirconium. These alloys strongly resist oxidation. Furthermore, as has been stated, these alloys have never been successfully prepared in any quantity with a high percentage of zirconium by the alumino-thermic reduction and only small beads of the metal could be picked out from the fused mass after the reaction had taken place. A number of variations were attempted in the mixture to get a good yield, but no satisfactory results were obtained. Larger charges and additions of fluxing agents may possibly give better yields.

An attempt was made to prepare ferrozirconium in the arc furnace. An arc furnace, which is shown in figure 3 (p. 117) was used in these trials to heat charges of zirkite, powdered iron, and fluorspar. Aluminum was added after the mass was fused, and a ferrozirconium containing a high percentage of silicon was prepared, which analyzed about 70 per cent iron, 20 per cent zirconium, and 10 per cent silicon. This alloy was hard and brittle. It might possibly be satisfactory for introducing zirconium as a scavenger into molten iron or steel, but other methods for the preparation of ferrozirconium are believed to work just as satisfactorily and possibly with greater ease. The yield of ferrozirconium under these conditions was only fairly good because much of the material stuck to the sides of the furnace. One point in favor of such a method for preparing ferrozirconium is that this alloy contained very little carbon.

NICKEL ALLOY.

An attempt was made to prepare one of the alloys described by Cooper^{39c}, consisting of nickel, zirconium, silicon, aluminum, etc., by Cooper's alumino-thermic reduction process, as follows:

One hundred and thirty-two grams of black oxide of nickel were mixed with 72 grams of zirkite and 64 grams of 200-mesh aluminum in a fire-clay crucible, which was packed in an insulator contained in a larger vessel. The top of the mixture was sprinkled with a little BaO_2 and the mass ignited with magnesium ribbon as usual.

The reaction was comparatively slow, but gave a good yield of the alloy described by Cooper. The average analysis of this alloy compares with that given by Cooper, as follows:

Comparison of analyses of nickel-zirconium alloy.

Analysis found:	Per cent.
Si -----	5.56
Zr -----	6.39
Al -----	8.31
Ni -----	79.74
Analysis of Cooper:	
Si -----	3.80
Zr -----	6.84
Al -----	8.36
Ni -----	81.00

Except for the silicon, the analyses check fairly well. With the Shore scleroscope the alloy shows a hardness of about 40, being considerably harder than nickel, so that it might be used for cutlery, if it does not prove too brittle.

CHAPTER XVII.—USE OF ZIRCONIUM DEOXIDE AS A REFRACTORY.

In the course of the investigation trouble was experienced in finding crucibles for use in the Arsem furnace. Aluminum oxide crucibles supplied with the furnace did not give trouble in melting down, but disintegrated and flew into pieces on continued heating at a high temperature, probably because of the binders used in making them being insufficient. A later batch of crucibles did not disintegrate, but cracked in the bottom and sides, allowing the molten charge to run out.

As ZrO_2 melts at a higher temperature, it was hoped that crucibles could be prepared that would serve better than the alumina. Many suggestions have been made on the preparation of zirconia ware and the use of various binders to prevent disintegration.

Pure ZrO_2 was first ground in the ball mill to a paste with water, and this paste was molded over a small wooden form. After the molds were partly dry they were taken off, further dried, and finally ignited. Trouble was experienced in removing the form because the ZrO_2 shrinks and clings to it. Crucibles thus made are porous and crack easily.

Through the courtesy of the Herold China & Pottery Co., of Golden, Colo., three small plaster of Paris forms were obtained in which crucibles were cast. These plaster of Paris forms were the same as were used for casting small porcelain crucibles for use in the chemical laboratory.

The zirconium oxide was ground with water in a ball mill until a fairly thin suspension of very finely divided oxide was formed. This was poured into the form, which absorbed water until the desired thickness of ZrO_2 was deposited. The excess of ZrO_2 suspension was poured away and the form and contents allowed to stand from one-half to two hours. The ZrO_2 crucible thus formed shrinks away from the plaster of Paris form, is lifted out and dried for some time at 100°C ., when it becomes firm and hard and can be handled without danger of breaking. Through the courtesy of the Herold China & Pottery Co. these crucibles were fired in their furnaces for three days with porcelain ware at about $1,600^\circ \text{C}$.

When pure ZrO_2 was used with pure water, the crucibles thus formed were crumbly and developed cracks on firing. Trial showed that much shrinkage of the crucibles could be obviated by first igniting the ZrO_2 to a high temperature before use, and that a binder was needed.

On later trials a little phosphoric acid or sulphuric acid was used in making the suspension of ZrO_2 . Crucibles made in this way from previously ignited oxide proved very satisfactory. There was still a shrinkage of about 30 per cent but the crucibles were nearly as hard as unglazed porcelain. When the grinding in the ball mill was thorough, the texture was uniform and as impervious as that of good porcelain. These crucibles withstood a higher temperature than the aluminum oxide crucibles furnished with the Arsem furnace; on ignition to a very high temperature they disintegrated much as the aluminum oxide crucibles had done.

Trials were made using a small percentage of MgO but no beneficial results were obtained and the magnesium oxide clung to the sides of the plaster of Paris mold so that the crucibles could not be easily removed.

The same difficulty was experienced in attempts to cast zirkite crucibles. Work was done, however, at the author's suggestion on pressing zirkite crucibles by the Denver Fire Clay Co., of Denver, good results being obtained.

Work on the preparation of ZrO_2 crucibles was not continued because of lack of time and material, but enough was accomplished to show that by the simple process of casting in plaster of Paris molds with the proper binder the crucibles would withstand temperatures in the Arsem furnace much in excess of $2,000^\circ \text{C}$. without melting or disintegrating.

CHAPTER XVIII.—BRIEF SUMMARY OF RESULTS OF WORK ON ZIRCONIUM.

The field covered during the investigation of zirconium has been very broad, and the conclusions that might be drawn from the individual experiments are so numerous that only a general summary can be given here. Many conclusions have been presented in the chapters on the various subjects discussed. Attention is called to the following points:

A complete bibliography of the literature on zirconium and its compounds is given in Part IV, pages 119 to 144.

A general historical discussion of the preparation, commercial uses, etc., of zirconium and its compounds is given in Part I, pages 5 to 43.

As the scope of investigation has been wide, all of the details of the various phases of the work have not, in every case, been studied as thoroughly as they might have been had more time been available. Some of the more important results of the experimental part of the investigation are as follows:

1. All of the known methods for the fusion or solution of zirconium ores have been tried either on a laboratory scale or on a semicommercial scale with quantities ranging up to 10 pounds. Good extractions of zirconium can be obtained by fusing either zirkite or zircon with caustic soda, soda ash, or mixtures of the two, or with niter cake, under the proper conditions. The treatment of zirkite with concentrated H_2SO_4 has been shown to yield good results. Zircons are much more resistant to H_2SO_4 or fusion agents and hence the extractions are poorer than with zirkite.

2. All of the known methods for the preparation of pure zirconium oxide have been tried, some of them on 1 to 10 pound quantities. For very pure salts, the quickest and most satisfactory method was to recrystallize the double fluorides of potassium and zirconium. This method serves well for chemically pure salts, but is entirely too expensive and tedious for commercial use.

The oxychloride method of crystallization works well only when the material is comparatively free of sodium, iron, and aluminum salts. When bisulphate or caustic fusions are used to render the ore soluble, the zirconium should be first precipitated to remove some of the impurities. The necessity of precipitation and of using concentrated HCl greatly lessens the value of this method for commercial uses.

The basic sulphate method of crystallization received especial attention in the hope that it could be combined with the sulphuric acid method of treatment of zirkite ore to yield a high-grade product at minimum cost. These trials were attended with much success and under proper conditions, zirconium oxide (99.84 per cent) can be prepared by this method for about 20 cents a pound (total cost of materials), as compared with 40 cents a pound by the cheapest of any other of the known methods. Some work on a commercial scale should still be done toward improving the yield of basic sulphates obtained from the sulphate solutions.

Several other methods of ore treatment for the production of ZrO_2 were developed, such as an application of the phosphate precipitation or the use of SO_2 for precipitating zirconium. With either the total cost for materials is about double that for the basic sulphate method.

3. Comparison of the various methods recommended for the quantitative determination of zirconium (the analytical data are given in Chapter XI) shows that sodium iodate gave incomplete precipitations and that SO_2 and sodium thiosulphate precipitated the zirconium quantitatively from pure chloride or sulphate solutions, but did not serve well for precipitation from solutions containing sodium or aluminum salts in quantity. Phenylhydrazine precipitates all of the zirconium and aluminum, but sometimes difficulties in washing the slimy precipitate caused errors. Iron and other impurities in this precipitate are difficult to remove by washing.

The phosphate method of precipitation gives good results if the total amount of phosphate, washed upon filter paper, is not more than 0.1 gram. Some authors have stated that the factor for the conversion of the ignited phosphate to the oxide should be less than 0.5, but good checking results have been obtained using the theoretical factor 0.518. The difficulties in the phosphate method are in washing the gelatinous phosphate precipitate and in completely igniting it.

The cupferron method yields very accurate results for iron and zirconium. Cupferron is the only precipitant that accurately separates zirconium from aluminum.

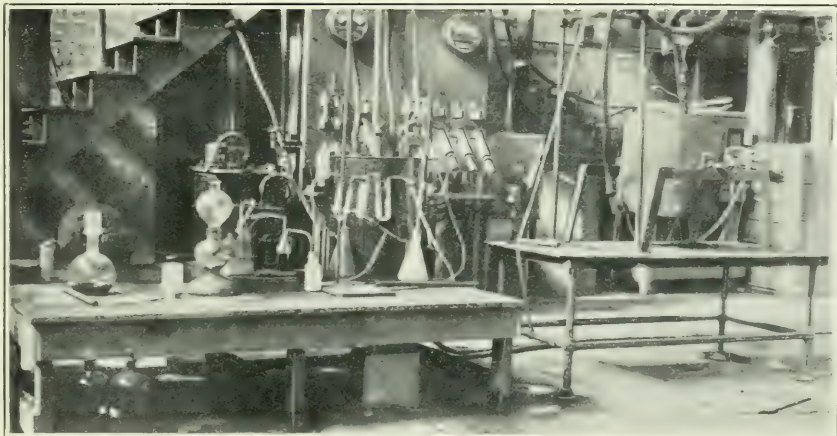
4. All of the methods listed in the literature except one have been tried for the preparation of amorphous zirconium. By the reduction of K_2ZrF_6 with sodium or aluminum amorphous metal has been obtained that yielded on analysis as high as 98 per cent zirconium, and compared favorably with any amorphous metal heretofore prepared. The reduction of ZrO_2 with Al, Mg, or Zn has never yielded high-grade amorphous zirconium, and reduction of K_2ZrF_6 with Mg, Zn, Pb, etc., has proved unsatisfactory. Amorphous zirconium has been prepared by the electrolysis of fused K_2ZrF_6 . Impure amorphous zirconium can be made directly from zirkite.

5. Coherent metal of 99.5 per cent purity has been made by aluminothermal reduction, by the vacuum-arc method, and also in the Arsem vacuum furnace by the interaction of K_2ZrF_6 and aluminum. Amorphous zirconium can be sintered into the coherent metal in an atmosphere of evacuated (1 to 2) pure, dry hydrogen, but can not be sintered in an atmosphere of evacuated air. Attempts to reduce ZrO_2 with carbon indicated that coherent zirconium could be obtained, but no metal of high purity was successfully prepared in this manner. Attempts to reduce ZrO_2 with metals other than aluminum were failures.

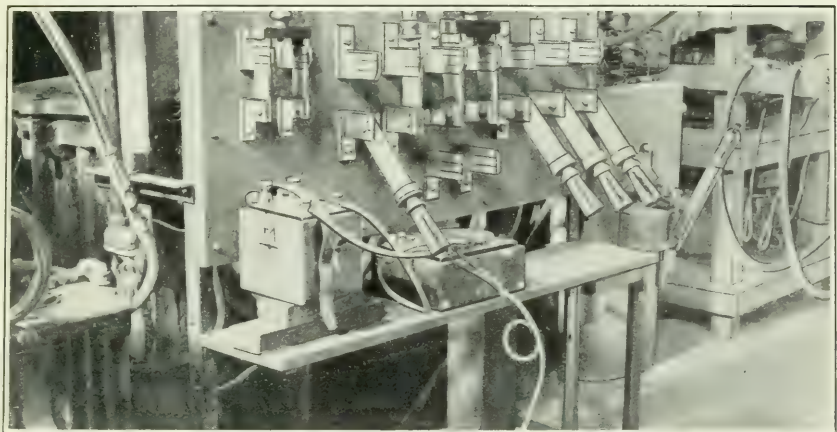
6. Investigation of the literature and analysis of the products obtained in experiments showed that the metal heretofore listed as crystalline zirconium was an alloy of zirconium and aluminum containing 70 to 75 per cent zirconium. An alloy of zirconium with silver was prepared. Several ferroalloys of varying composition were made which, contrary to previous statements that zirconium alloys containing 60 to 90 per cent zirconium were ductile and malleable, proved very brittle and very hard. One of the nickel alloys, which has been suggested for use in cutlery and high-speed cutting tools, was hard and fairly resistant to acid.

7. Crucibles prepared from zirconium oxide proved superior for high-temperature work to any crucibles procured on the market.

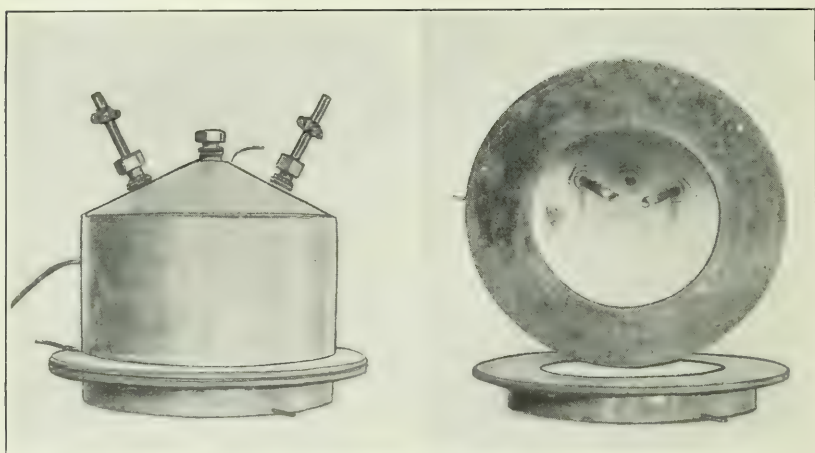
8. Only two forms of zirconium were prepared in this work, namely, the amorphous and coherent metal. No zirconium metal showing individual crystals of a structure similar to that of the zirconium-aluminum alloy has been prepared. No study of the coherent metal was made with the use of the microscope. However, such an investigation together with proper heat treatments in order to make a more ductile form of this metal for the production of wire, sheet, etc., might yield very interesting results. Attempts to prepare graphitoid zirconium were failures, and it is not believed that this variety exists. The amorphous metal can be easily converted into the coherent metal in the presence of aluminum in an atmosphere of evacuated hydrogen.



A. LABORATORY ARSEM FURNACE AND SWITCHBOARD.



B. SWITCHBOARD USED WITH ARSEM FURNACE.



VACUUM ARC-FURNACE.

PART III.—FURNACES USED.

THE ARSEM FURNACE.

The Arsem vacuum furnace^j used in the experiments outlined above was of the small vertical type, taking a maximum of 15 kilowatts. A maximum of 250 amperes was used with 60 volts, which yielded a maximum temperature of about 3,000° C. A photograph of the furnace is reproduced as Plate I, A. The furnace consists of an iron vessel, made airtight, which incloses a graphite helix held in place by water-cooled electrodes. This vessel, which has a mica window for observations and a tube for evacuating the atmosphere within, is immersed in water.

The furnace held a crucible having a content of about 5 cubic inches. Vacuum was obtained by an electrically driven rotary oil pump that would give a vacuum of less than 1 mm. in the entire apparatus in a very few minutes.

Current was supplied from a 2,200-volt, single-phase generator, the switchboard being arranged with suitable transformers so that 8 to 80 volts could be obtained in steps as required. The Arsem furnace circuit was equipped with a portable transformer and wattmeter, so that the kilowatts used in the furnace could be read at any time during operation.

Plate I, B, shows the switchboard. Figure 1 is a diagram of the wiring.

In making a run with the Arsem furnace, after the apparatus was evacuated and water was circulating through the brass tube electrode holder, the current was usually started with 40 volts; the switches were set as shown in B, and the adjustable transformer set for the lowest voltage—about 2 kilowatts. By changing the transformer the voltage was gradually raised until the desired temperature was

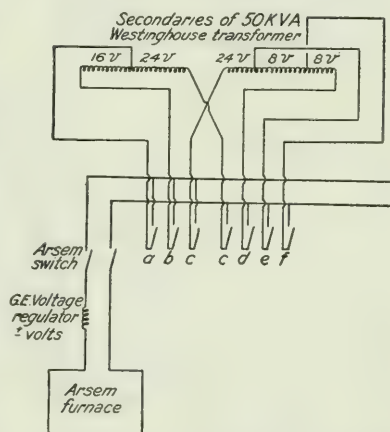


FIGURE 1.—Diagram of the wiring for the Arsem or arc furnace. Forty-volt connection of main transformer is used. Voltage is adjusted with feeder regulator; continuous change from 40 to 25 volts.

^j For a more detailed description of this furnace, see Bull. 4898B of the General Electric Co., Schenectady, N. Y.

attained. Generally it takes about 20 minutes to raise the temperature to $2,000^{\circ}\text{C}$. From a curve made by plotting the kilowatts consumed in the furnace against the temperature, the temperature can be approximately read for any current consumed. During the experiment the reaction is observed through the mica window at the top of the furnace.

THE VACUUM ARC FURNACE.

Plate II shows the vacuum arc furnace devised for the work. The interior of the furnace is about 1 foot high and 1 foot in diameter,

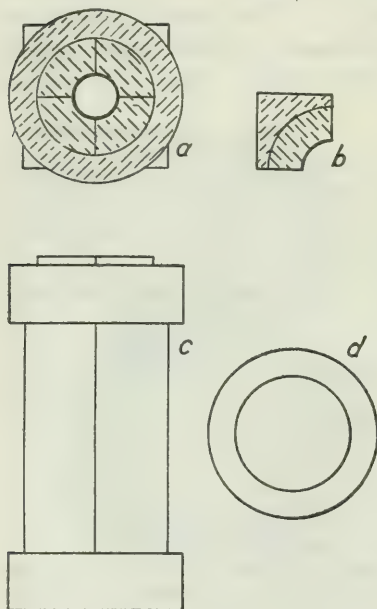


FIGURE 2.—Diagram of form used for pressing zirconium-aluminum alloy. *a*, end view, four sections in place; *b*, end view of a quarter section; *c*, side view; *d*, iron ring for holding sections in place.

and made of two parts, a top and a base, both of which are jacketed for water-cooling. The electrode holder consists of brass tubing arranged for water-cooling and held in place by insulated stuffing boxes that can be moved up and down, as the arc demands, while the vacuum is maintained. When the furnace is in operation the top is firmly bolted to the base, the joint being made airtight with gasket rubber. The furnace is fitted with a mica window for observing the reaction within.

In work with the arc vacuum furnace means had to be developed for pressing the zirconium-aluminum alloy into sticks which were fastened into the electrode holders. The apparatus used consisted essentially of a quartered steel block form through which a hole had been bored, the quarters

of the form being held together by steel rings. Steel plugs of various lengths were inserted successively in the hole which had been filled with aluminide and pressed down by means of a screw press. Pressure was exerted on alternate ends until the aluminide had been compressed enough to adhere closely. After the sticks had been removed from the form they were heated to nearly $1,000^{\circ}\text{C}$. in an evacuated atmosphere of pure dry hydrogen. This heating partly sintered the metal and made the sticks solid conductors which were

ready for use in the arc furnace. Figure 2 is a diagram of the form used for pressing.

ARC FURNACES FOR FERRO ALLOYS.

Figure 3 shows a diagram of the furnace used for the experimental production of zirconium ferro alloys. This consisted of a sheet-iron container packed with a lining of magnesite and tar, *m*, and so hung that the charge could be poured out after fusion by use of the handle,

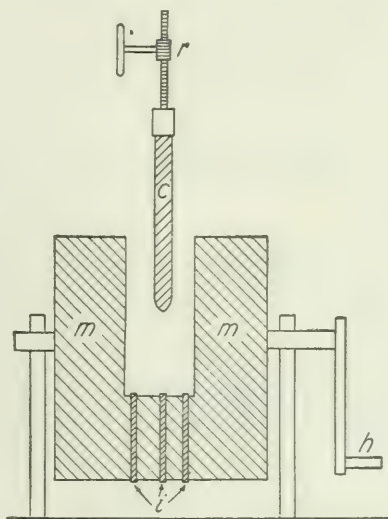


FIGURE 3.—Cross section of arc furnace for ferro alloys.

h. The lower connections were made by means of iron spikes, *i*, and the upper connections consisted of a $1\frac{1}{2}$ -inch strip of graphite, *c*, which could be raised or lowered at *r*. The interior of the furnace was about 6 inches in diameter and 12 inches deep.

PART IV.—BIBLIOGRAPHY OF ZIRCONIUM AND ITS COMPOUNDS

FOREWORD

The following bibliography, collected in the course of investigations on the preparation and properties of zirconium, has been made as complete as possible with the journals at hand. The material is arranged under the following general headings:

- I. Zirconium minerals.
- II. Preparation, properties, and uses of zirconium salts.
- III. Analytical chemistry of zirconium.
- IV. Zirconium metal.
- V. Zirconium alloys.

The subject matter under each subdivision has been arranged in alphabetical order by the authors in order to avoid much cross filing of references.

Some of the references were taken from textbooks or journals not available at present. A few of the titles to papers do not state the subject matter of principal importance on the subject for which they have been listed here.

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